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TREATMENT OF WATER FOR ICE MANUFACTURE

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION

UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE UTILITIES RESEARCH COMMISSION

BY

DANA BURKS, JR.

BULLETIN No. 219

ENGINEERING EXPERIMENT STATION

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UNIVERSITY OF ILLINOIS
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ENGINEERING EXPERIMENT STATION

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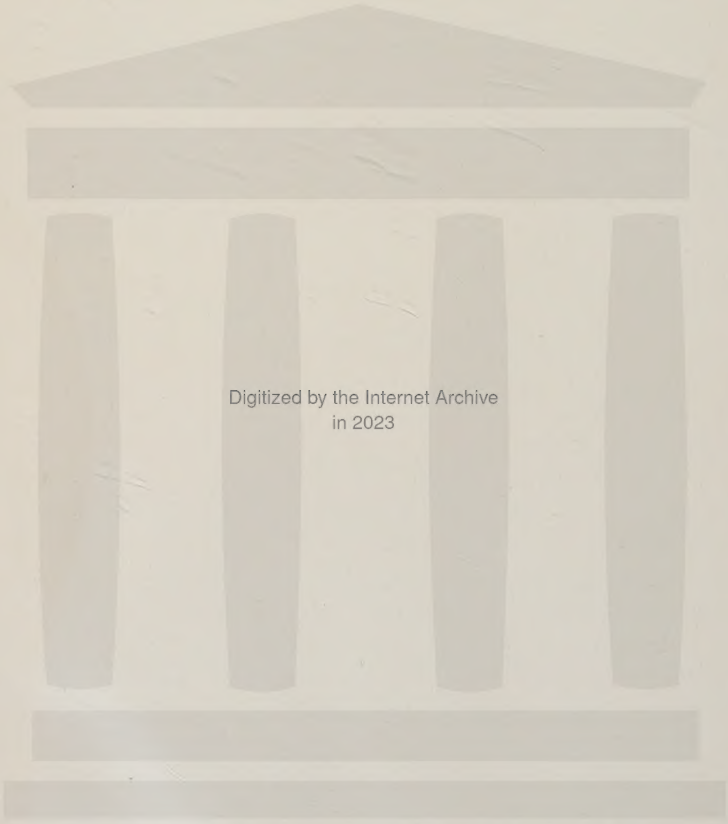

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TREATMENT OF WATER FOR ICE MANUFACTURE

I. Introduction

1. *Introduction.*—The production of manufactured ice has progressed so rapidly in recent years that it now ranks as one of the major industries of the country. The industry is still composed, however, of manufacturing units operating independently and locally. The problems of this decentralized group, therefore, warrant careful and exhaustive investigation especially since the high level of public health itself depends upon their efficient operation. This is particularly true concerning problems effecting efficient operation, since economies once established rapidly find expression in increased service.

Recognized as one of the most important factors contributing to economic operation is complete electrification. It has been demonstrated, for example, that a ton of coal burned in a steam driven ice plant will produce from four to six tons of ice, while this same fuel consumed in a central generating station produces sufficient electric power to manufacture from fifteen to eighteen tons when utilized in an electrified plant. In many plants, however, factors exist which render the use of electric power impossible. The steam generating equipment, for example, may have been so recently installed that the depreciation loss incurred by its removal cannot be economically absorbed.

The one factor which even more fundamentally renders electrification impossible, however, is the quality of water available as an industrial supply, for in the electrified plant natural water is the only source available for the production of ice. As such waters invariably contain dissolved salts, difficulty in the production of a desirable quality of ice is encountered when the salt concentration becomes excessive. The quality most desired in manufactured ice is a high degree of transparency. When the salt concentration is high, however, opacity results.

The need for fundamental research in this specific field was suggested to the Engineering Experiment Station of the University of Illinois by Mr. A. J. Authenrieth, vice president in charge of ice and refrigeration of the Middle West Utilities Company. As a result, the Utilities Research Commission, representing the Chicago Rapid Transit Company, The Commonwealth Edison Company, The Chicago North Shore and Milwaukee Railroad Company, The Midland United Company, The Middle West Utilities Company, The Peoples Gas, Light and Coke Company, and The Public Service Company of

Northern Illinois, in July, 1928, instituted a coöperative project in the Engineering Experiment Station of the University of Illinois to be concerned with the specific water problems affecting the manufactured ice industry as a whole. This investigation has as its scope a general survey of raw water sources available throughout the entire United States for the production of manufactured ice, and the development of methods of water treatment whereby each of these water supplies may become available for the production of the highest quality ice in completely electrified plants.

2. *Advisory Committee.* — The members of the Committee appointed by the Utilities Research Commission to act in an advisory capacity during the investigation were: Mr. A. J. Authenrieth, vice president in charge of ice and refrigeration of The Middle West Utilities Company, chairman; Mr. E. A. Armstrong, manager of power sales, Public Service Company of Northern Illinois; Mr. C. J. Carlson, refrigerating engineer of The Commonwealth Edison Company; and Mr. J. B. Reynolds, director of industrial development of The Middle West Utilities Company.

3. *Acknowledgments.*—The investigation was conducted as part of the work of the Engineering Experiment Station of the University of Illinois at Urbana under the administrative direction of Dean M. S. Ketchum, Director of the Station.

Particular acknowledgment is made to Prof. D. B. Keyes, head of the Industrial Chemistry Division of the Chemistry Department of the University of Illinois, under whose personal direction the investigation was conducted. His continued coöperation, invaluable suggestions, and untiring interest have contributed more than any other factor to its successful completion.

Acknowledgment is made for the generous use of plant operating facilities and equipment offered by Mr. D. C. Dodds, president, and Dr. F. C. Dodds, manager of the Twin City Ice and Cold Storage Company of Champaign, Illinois. Acknowledgment is also made to Mr. C. H. Stipes, chief engineer of this concern, who materially assisted with practical suggestions which, in any project of this type, are of utmost importance. The plant operators, Mr. C. E. Cunningham and Mr. Paul Lorenz, also rendered valuable service in the capacity of observers during continued plant operation.

Acknowledgment is made to Mr. A. J. Authenrieth, whose continued interest has served to keep the investigation in touch with the active problems of the industry.

FIG. 1. OPAQUE ICE FORMATION—EFFECT OF WHITE SHELL

Acknowledgment is made to the UNITED STATES GEOLOGICAL SURVEY for the cordial coöperation rendered by the head of the Quality of Waters Division, MR. W. D. COLLINS.

4. *Outline of Investigation.*—The chief difficulty arising from the use of natural water supplies in the production of manufactured ice has been stated to be an objectionable appearance. In the first manufactured ice plants the mechanical units were powered by means of steam, the exhaust steam being condensed, and the distilled water thus recovered was quietly frozen in cans submerged in a brine maintained at a sufficiently low temperature to insure a rapid rate of freezing. Under ideal conditions the ice was invariably clear and transparent. Consequently, the consumer came early to associate purity with transparency. This association was augmented by the fact that in the previous era, wherein use had been made of natural ice, the practice had been rigidly followed of removing the top opaque layer which

FIG. 2. OPAQUE ICE FORMATION—EFFECT OF "FLOWERS" OR "BUTTS"

contained all of the refuse and objectionable matter inherent in this mode of production, and of storing only the clear ice which lay beneath.

Under modern production methods wherein electric power is used to produce the required refrigeration no economic source of distilled water is longer available. The cost of its production for the freezing process alone renders this procedure impossible. Recourse must therefore be had to the use of local water supplies, which invariably contain dissolved salts. When such supplies are frozen according to the procedure of quiet freezing, which yielded satisfactory results in the distilled water process, densely opaque ice invariably results. Therefore, in the electrified manufacturing process, the water undergoing freezing is agitated by means of compressed air, a practice which may well have originated from observations made in the case of natural ice formed in rivers and streams wherein the water was constantly in motion during the freezing process, and from which remarkably clear ice was often produced even though the water being frozen contained

FIG. 3. OPAQUE ICE FORMATION—EFFECT OF COMPLETE OPACITY

considerable quantities of dissolved salts. In any event the idea has become established that if ice as it is formed is constantly and vigorously bathed with the solution remaining unfrozen the dissolved salts, assumed to occasion opacity by separating as solids along with the ice, will be washed away from the steadily forming ice surface.

It was soon determined, however, that when the initial concentration of the dissolved salts in the water was high the production of transparent ice became increasingly difficult and in many cases impossible; a white opaque shell encased the outside of the cake either completely or in part, large white opaque "flowers" or "butts" occurred in the interior of the cake, or the cake was opaque throughout. Representative examples of these conditions are shown in Figs. 1, 2, and 3. In those cases where the production of manufactured ice from the natural water supplies available is impossible, recourse must be had to the more expensive procedure involving distillation, thus rendering

TABLE 1

ANALYSES OF TYPICAL SODIUM BICARBONATE WATERS

Ionic Constituents		Concentration, parts per million				
		(1)	(2)	(3)	(4)	(5)
Sodium	Na	186	264	80	241	143
Calcium	Ca	3	6	6	6	6
Magnesium	Mg	2	0	2	5	2
Bicarbonate	HCO_3	458	557	202	440	415
Chloride	Cl	24	57	15	50	2
Sulphate	SO_4	12	52	4	138	5
Iron and Aluminum	R_2O_3	..	1	..	..	..
Silica	SiO_2	..	12	..	..	..
Hypothetical Combinations						
Magnesium bicarbonate	$Mg(HCO_3)_2$	13	0	13	29	15
Calcium bicarbonate	$Ca(HCO_3)_2$	14	25	25	24	24
Sodium bicarbonate	$NaHCO_3$	600	741	250	546	530
Sodium chloride	NaCl	40	94	25	76	6
Sodium sulphate	Na_2SO_4	18	77	6	202	7
Total Solids		685	949	319	877	582

(1) Well at Smithville, Virginia
(2) Well at Crisfield, Maryland
(3) Well at Long Beach, California
(4) Well at Waco, Texas, (part of municipal supply 1921)
(5) Well at Pitcairn, Pennsylvania

the application of electric power unavailable. In many sections of the country electrification cannot at present be accomplished due solely to the quality of the water supplies locally available. Some idea of the economic aspect of this condition is gained when it is considered that of the 53 544 351 tons of ice produced in the United States during 1929,* representing a gross income of $394 086 423,† approximately 32 per cent was manufactured in steam driven distilled water plants.‡

Since the present investigation has as its aim the development of methods whereby all industrial water supplies may be rendered available for use in electrified ice plants, it early became apparent that it would be necessary to classify the water supplies of the country according to some general characteristic. It was felt that what this procedure lacked in offering specific methods for each local condition it would gain by indicating possibilities in a general field of application. The characteristic chosen was the predominating dissolved sodium salt content of the solution. This classification holds even in

*National Association of Ice Industries. Private communication.

†Calculated on the basis of the grand average price for all ice sold in 1928—$7.36 per ton. Ice and Refrigeration Blue Book and Buyers Guide, 10th Ed., p. 39, Nickerson and Collins, Chicago.

‡Estimated from 1927 data. Ice and Refrigeration Blue Book and Buyers Guide, *loc. cit.*

the case of those waters high in calcium and magnesium, since these constituents may either be removed in the form of their salts by the application of calcium hydroxide (common lime softening) or may be exchanged for sodium by means of either sodium carbonate (soda ash) or sodium zeolite. The three types of waters to be studied, therefore, were sodium bicarbonate or carbonate, sodium chloride, and sodium sulphate.

The sodium bicarbonate type, typical analyses of which are shown in Table 1, was arbitrarily chosen as the first to be studied. It is seen to be characterized by the presence of high concentrations of sodium and bicarbonate ions and low concentrations of calcium and magnesium ions in equilibrium with varying though comparatively low concentrations of sulphate and chloride ions. Because it contained the highest concentration of dissolved salts and as such would occasion the greatest difficulty in the production of an acceptable grade of ice, the water found at Crisfield, Maryland, was used as the type example throughout the investigation.

Waters of this type, according to Collins and Howard,* are characteristic of the well supplies found in many parts of the United States. They seem to be confined to no particular district other than being commonly encountered in the territory designated as the Atlantic Coastal Plain, a province extending from southern New Jersey in a strip of varying width along the Atlantic and Gulf coasts, to Mexico, excluding Florida.

It was early determined that no accurate correlation existed between small samples of water frozen in the laboratory and those frozen under plant-scale conditions. As a result, plant-scale experimental freezing equipment and operation was offered by the local ice plant. The conclusions reached in this investigation have, therefore, been based upon results obtained from practical operation. This has, of course, an inherent disadvantage in that operating conditions could not at all times be carefully controlled, being of necessity those of the plant offering facilities. At definite periods during seasonal operation certain power load features render it advisable for the refrigerating units of an operating plant to be shut down during the peak load hours, thus resulting in variable brine temperatures. These disadvantages are, however, felt to be more than balanced by the fact that successful results have been obtained in spite of them, thus rendering the result more applicable to actual plant operating conditions as generally encountered.

*Collins and Howard, Ind. Eng. Chem., vol. 19, p. 623, 1927.

As a result of the investigation two distinct methods have been developed whereby any characteristic sodium bicarbonate water source may be used in the production of marketable manufactured ice. The first is based upon definite modifications in present manufacturing practice, places particular stress upon obtaining greater efficiency of air agitation during the freezing process by means of a new type of ice can, and makes no attempt to reduce the concentration of salts dissolved in the water prior to the freezing operation. The second introduces a new method of chemical water treatment prior to the freezing operation, whereby the total salt concentration of the water may be reduced to such an extent that standard operating conditions and equipment may be utilized. The two methods will be separately described in detail.

II. Mechanical Method for Treatment of Waters High in Sodium Bicarbonate

5. *Formation of Opaque Ice.*—It has been stated that in the electrified ice plant natural water supplies must be frozen and that the dissolved salts which these supplies contain occasion the formation of ice which is opaque unless special precautions are taken. If these supplies are allowed to freeze quietly according to the procedure followed when distilled water is frozen the ice is uniformly opaque throughout. To overcome this difficulty the freezing of water containing dissolved salts is accompanied by agitation of the water with compressed air. The need of agitation follows as the result of the following considerations:

The water to be frozen in actual plant operation is placed in sheet metal cans which are in turn immersed in a brine solution the temperature of which is maintained as much below 32 deg. F. as possible in order to reduce to a minimum the time required to freeze completely the contents of the can. The water in the metal container is therefore subjected to an extremely high rate of cooling on entering the brine and a layer of ice quickly forms at the four sides and bottom. The formation of a layer of ice one inch thick on the walls of the ice can during the first hour of freezing, a condition observed to exist under actual conditions at a brine temperature of 16 deg. F., represents freezing 27 per cent of the water originally present in a standard 400-lb. can. Since the ratio between the heat conductivities of ice and steel is $\frac{0.004}{0.114}$ or 0.03, the rate of cooling decreases rapidly as additional ice

is formed, and fifty hours are required to freeze completely the remaining 73 per cent of water in the can.

When the temperature of a solution being cooled reaches a point where ice is formed two opposing tendencies are in operation, namely, the rate at which heat is absorbed from the solution and the normal diffusion of the dissolved salts. A high rate of heat absorption which results in a rapid formation of ice tends to concentrate locally the salts dissolved in the unfrozen solutions at the ice surface, due to removal of the solvent water as ice. Since a concentration gradient is thus established in the solution a homogeneous concentration tends to be re-established by diffusion of the dissolved salts. However, where any marked difference exists between the heat absorption and diffusion rates, as when the can is first immersed in the brine, the latter must be materially reinforced if a homogeneous condition is to be maintained. In actual practice this is accomplished by agitation resulting from compressed air blown into the solution. Air is alone available for this purpose since the physical conditions under which the agitation must operate necessitate a mechanical application which is both positive and flexible and yet readily disengaged from the finally frozen block of ice.

If the agitation afforded by the use of air is not sufficiently effective in reinforcing the rate of diffusion opaque ice will form at the outer sides and bottom of the ice cake where localized salt concentration, due to rapid ice formation, attains a value which prevents the subsequent formation of transparent ice crystals. This follows as a result of the conclusions presented in Appendix A which state that for every solution there exists a definite concentration of salt or salts dissolved in the unfrozen solution further concentration of which by the separation of ice results in the formation of ice crystals which are opaque.

Obviously the necessity for effective agitation is greater as the initial concentration of dissolved salts increases, since the critical concentration occasioning opacity becomes more readily attained. Also the need for agitation increases as the brine temperature is lowered since under these conditions the rate of heat absorption is materially increased.

As ice progressively forms in from the sides and bottom of the ice can, however, the temperature gradient existing between the surface of the solid phase and the water to be frozen gradually decreases. At first this phase consists solely of the thin metal layer of the can wall. The heat capacity of the metal being high a rate of heat absorption

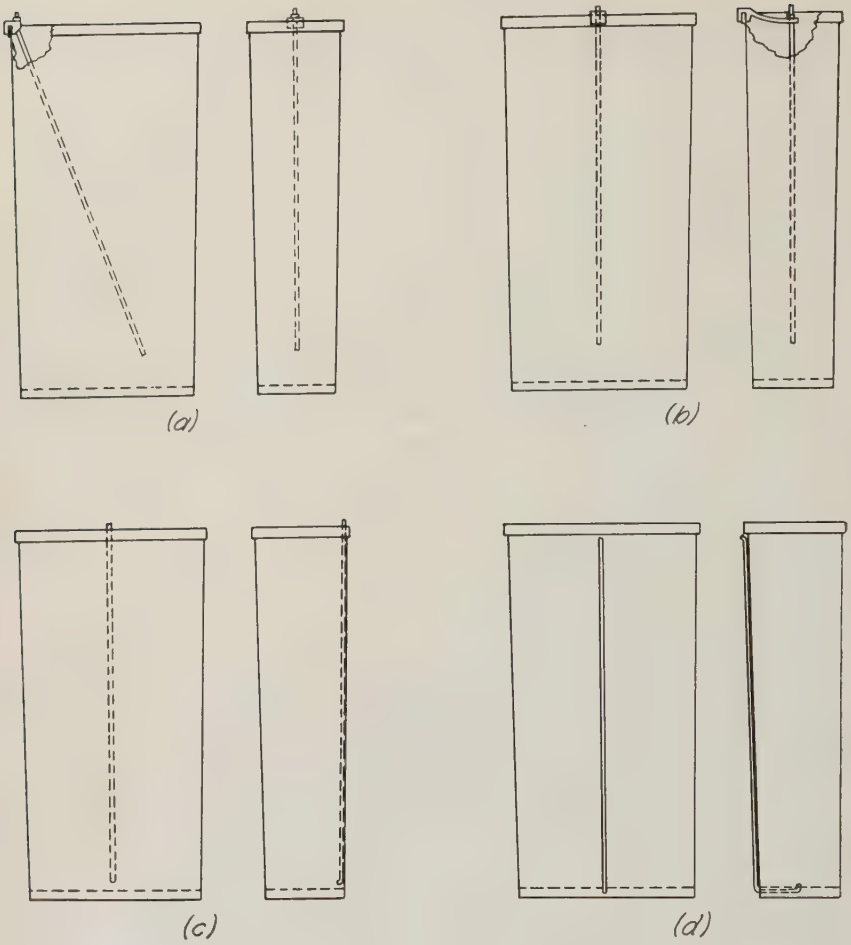

FIG. 4. METHODS OF APPLYING AIR FOR AGITATION IN STANDARD CAN DESIGN

results which is exceedingly great as compared to that resulting when the solid phase consists of the metal wall upon which is superimposed a gradually increasing layer of ice. Thus the heat conductivity of the solid phase rapidly decreases, as does the rate of cooling. Therefore, the need for extremely efficient air agitation exists only until a layer of ice has been formed sufficient to lower the rate of cooling to a point where a homogeneous concentration in the unfrozen solution may be maintained by a smaller volume of air less effectively applied. Under these conditions opacity will result only when the homogeneous core

FIG. 5. ICE FROM TYPICAL SODIUM BICARBONATE WATER AT CRISFIELD, MARYLAND
Standard freezing procedure employed.

water remaining unfrozen has reached the critical concentration. At this point the core water must be removed and replaced by a fresh supply of the water originally used.

6. *Present Standard Freezing Procedure.*—Although there are numerous operating systems being used in the ice industry at the present time there is still sufficient similarity between them to allow a general statement to be made which arbitrarily establishes an average procedure characterizing present standard operation. The water is frozen in cans of either 300 or 400 lb.* capacity immersed in a brine the average temperature of which is 16 deg. F. Air for agitation (either high or low pressure) is supplied to the water being frozen through

*In the experimental work to be described later the 300-lb. cans used had the dimensions 11 in. x 22 in. x 49 in. and the 400-lb. cans the dimensions 11 in. x 22 in. x 60 in.

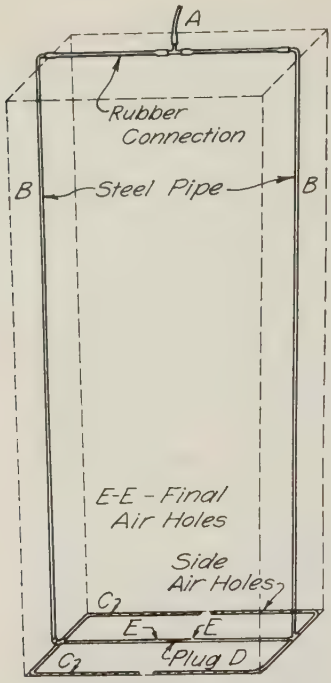

Fig. 6. Experimental Air Agitation Unit

small air tubes attached to the cans according to two distinct plans. In the first the air is allowed to enter through an auxiliary metal tube as indicated in Fig. 4a and Fig. 4b. This tube, suspended in the can by means of an auxiliary support, delivers the air to a central point approximately six inches above the bottom. The tube is then either allowed to freeze into the block of ice, to be subsequently removed by means of a so-called thawing needle carrying hot water and capable of passing down through the air tube, or is removed before the cake has finally frozen solid. In the second type the air tube is made an integral part of the can as shown in Fig. 4c and Fig. 4d, the air entering the can through a single hole located at the bottom, either at one side (as in c) or in the center of the bottom (as in d). The volume of air used per can varies from 0.1-0.3 cu. ft.* in the case of high pressure installations to 0.4 cu. ft. per min. in the case of low pressure systems employing blowers.

The agitation resulting from such application is characterized by the fact that the air enters the water from a single point and passes

*Throughout the bulletin all air volumes have been reduced to standard conditions, namely the volume measured at 32 deg. F. and 14.7 lbs. per sq. in. (abs.).

to the surface in large bubbles, the active zone of agitation existing in the form of an inverted cone whose apex corresponds to the point of entry. Such application unquestionably leaves a considerable area at the bottom and bottom sides of the can in a comparatively unagitated condition, wherein localized concentration of dissolved salts readily occurs. When the Crisfield water for example was frozen at 16.5 deg. F. in a 400-lb. can of the type shown in Fig. 4a and agitated by 0.2 cu. ft. of air per min. the result was that shown in Fig. 5. The ice is seen to be characterized by an extremely heavy veil practically encasing the cake and an exceedingly thick core. Ice possessing such appearance represents an entirely unmarketable product. A similar product would have resulted in the case of any of the standard can installations under the same operating conditions.

7. *Development of New Ice Can Design.*—The inability of standard can design to effectively agitate solutions possessing the initial salt concentration existing in the case of the Crisfield water led to the development of a new type of ice can. Experience clearly indicated that more effective agitation was needed at the extreme sides of the can during the initial freezing period while the rate of cooling was excessively great.

The experimental unit finally developed to accomplish this purpose consisted of a standard 400-lb. can containing a removable air header the construction of which is shown in Fig. 6. By means of such design air is conducted from the air laterals through two air tubes *B* to a bottom air header *C* which is perforated by a series of small holes spaced approximately one inch apart. These same tubes *B* also supply air to two holes *E* centrally located at the bottom. The plug *D* separates the header into two distinct units.

The experimental can was designed to operate as follows: Sufficient air, on being forced into the bottom header, causes an evenly distributed chain of bubbles to rise from all perforations. Effective agitation is thus afforded to the solution at the extreme sides of the can where the greatest rate of cooling occurs when the can is immersed in the brine. The first formation of ice thus occurs from a solution wherein the increased concentration of salt occasioned by the separation of ice is rapidly dissipated by the normal diffusion tendency aided by an active and positive mechanical agitation. With sufficient air issuing from the perforated header no marked increased concentration of dissolved salts results, subsequent ice formation thus occurring from a homogeneous unfrozen solution. As the formation of ice proceeds

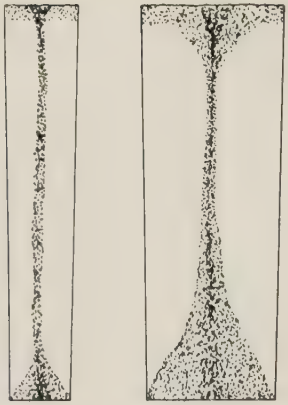

FIG. 7. BOTTOM OPACITY RESULTING FROM IMPROPER APPLICATION OF AIR AGITATION

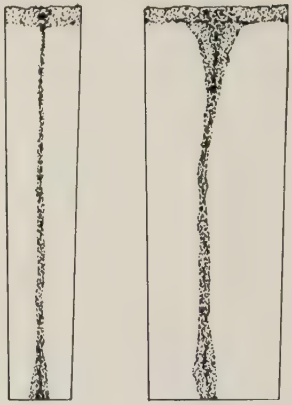

FIG. 8. BOTTOM OPACITY RESULTING FROM PROPER APPLICATION OF AIR AGITATION

from the sides, thus decreasing the heat conductivity of the total solid phase, a point is finally reached at which the rate of cooling becomes so reduced that opaque ice formation is prevented with not only a much smaller volume of air but also by the smaller volume entering the can solely from the holes located centrally in the bottom.

The continuance of agitation from the outer header longer than necessary is undesirable due to the fact that when the ice cake becomes completely frozen the channels through which the final air passes into the core freeze as an air foam and therefore subsequently appear opaque. If the final air is allowed to enter the can from the outside header until the end of the freezing operation or if, in fact, its entrance from the outside header is continued longer than necessary to prevent the formation of an opaque shell, air channels are maintained from all of the outer holes and the amount of bottom opacity resulting in the ice cake is comparatively large as indicated in Fig. 7. If, however, the reduced volume of final air is allowed to enter the can from the centrally located holes the area encompassing the final opaque foam is small as indicated in Fig. 8. Therefore, a distinct advantage exists in any procedure by which the air is prevented from entering the can from the side header as early as possible.

When the volume of air is decreased the resistance offered by the encroaching layer of ice to air entering the can from the side header becomes sufficient to effectively plug the holes contained therein and prevent further agitation from this source. All of the air thereafter

TABLE 2

COMPOSITION OF CRISFIELD WATER WHEN BICARBONATE CONTENT IS NEUTRALIZED TO SULPHATE

Ionic Constituents		Concentration, parts per million
Sodium	Na	264
Calcium	Ca	6
Sulphate	SO_4	490
Chloride	Cl	57
Hypothetical Combinations		
Sodium sulphate	Na_2SO_4	703
Sodium chloride	NaCl	94
Calcium sulphate	$CaSO_4$	21
Aluminum oxide	Al_2O_3	1
Silica	SiO_2	12
Total Solids		831

enters from the centrally located holes, thus supplying sufficient agitation to the core water throughout the remainder of the run. When ice formation at the four walls and bottom of the can finally coincides air agitation is automatically stopped. The can is then placed in a "dipping vat" containing warm water, the ice melts slightly at the sides and bottom, and the cake becomes free to be removed. In the thawing operation the side air header is cleared of any ice which may have formed due to an influx of water into the header when the air supply is reduced; this thawing action continues when the empty can is refilled with the next charge of water to be frozen.

8. *Experimental Results Using New Ice Can.*—The result of using this type of air agitation in the case of the Crisfield water was entirely successful. Since it was determined, however, that sodium bicarbonate waters exhibited less tendency to form opaque ice if the bicarbonate content was converted to sulphate* by means of either sulphuric acid or alum, neutralization prior to the freezing process was consistently practiced. The composition of the water actually subjected to freezing was therefore in all cases that indicated in Table 2. It is obvious that whereas the water originally studied was of the sodium bicarbonate type the water actually investigated was characterized by a predominating concentration of sodium sulphate. The results, therefore, apply in the case of both types.

*This evidence exemplifies a current assumption that whereas the total salt concentration is by far the chief factor in the production of opacity, the individual salt constituents or ions in the solution exert a distinctly specific effect. This point is further discussed in Appendix A.

FIG. 9. ICE FROM NEUTRALIZED CRISFIELD WATER FROZEN IN EXPERIMENTAL AIR AGITATION UNIT

Auxiliary air was used and a large core was removed.

When the neutralized Crisfield water was frozen in the experimental unit described in Section 7, the resulting product was that shown in Fig. 9. Agitation was afforded by 1.3 cu. ft. of air per min. for the first two hours, followed by 0.3 cu. ft. per min. for the remainder of the run. The air was supplied from an air lateral in which the pressure was 20 lb. (gage). The brine temperature was 15 deg. F. Two cores were removed, one when the volume of unfrozen solution was 10 gallons, a second when the volume was 1 gallon. The cores were in each case replaced with water having the same composition as that originally used.

Numerous samples of the Crisfield water, some 2000 gallons of which were shipped to the University for experimental purposes, frozen under similar conditions yielded results which were strictly compar-

FIG. 10. ICE FROM DISTILLED WATER FROZEN IN STANDARD CAN WITH STANDARD AIR AGITATION

able. In order to indicate fully the quality of ice produced by this method a sample of distilled water frozen under standard operating conditions is shown in Fig. 10, while in Fig. 11 is shown a sample of the ice regularly produced at the local ice plant.

Aside from the use of a new type of air agitation the proposed method is seen to be additionally characterized by the use of a large volume of auxiliary air for agitation and the removal of a large volume of core water. Both procedures depart somewhat radically from so-called standard procedure. In Appendix E it will be shown, however, that the use of the auxiliary air proposed increases the cost of production by only $0.005 per ton.

On the basis of the conclusions reached in Appendix A concerning the formation of opaque ice it follows that although the formation of

FIG. 11. ICE REGULARLY PRODUCED AT LOCAL ICE PLANT

an opaque shell may be prevented by the use of effective agitation during the first hours of the freezing period, no amount of agitation will prevent the formation of opaque ice when the homogeneous core water has reached a definite critical concentration. Since this concentration is in each case a specific property of the solution being frozen the amount of core water which must be removed when this concentration is reached will depend upon the initial concentration and composition of the dissolved salts. The power loss occasioned by the removal of core water as proposed is, however, shown in Appendix B to increase the cost of production by only \$0.016 per ton or 0.5 per cent.

Thus, although radical departures from standard practice, the modifications proposed are seen to possess no marked economical disadvantages. A comparison of approximate cost distribution for the

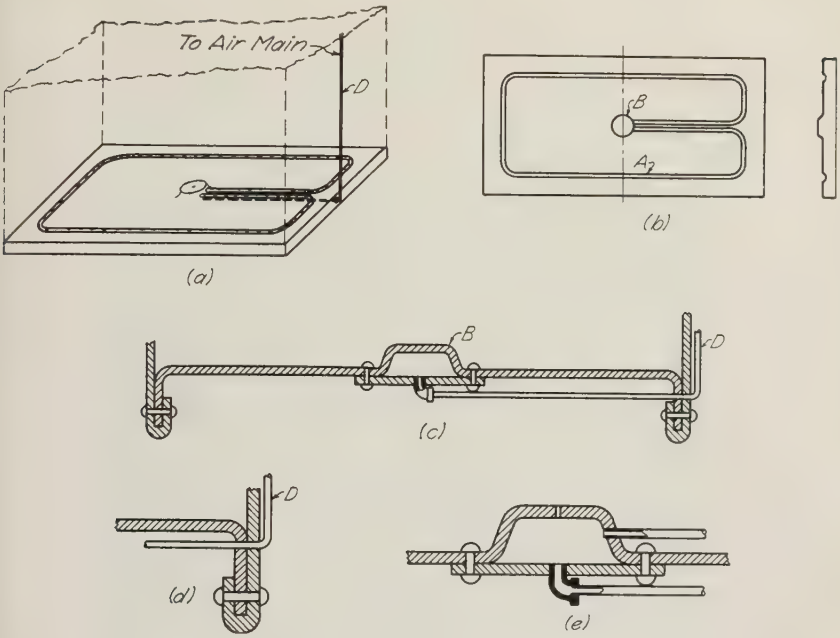

FIG. 12. DETAILS OF ICE CAN MANUFACTURED ACCORDING TO SPECIFICATIONS DEVELOPED DURING INVESTIGATION

method and that obtained in the case of standard procedure is shown in Appendix E.

9. *Specifications for Proposed Ice Can.*—Two types of can construction to meet the requirements of the proposed method have been developed in the 300-lb. can size. One is embodied in a test can prepared and submitted by one of the can manufacturing companies on the basis of suggested specifications. The other, which more nearly meets the requirements of the method but has not as yet been subjected to critical examination from the standpoint of manufacturing details, has been fabricated in the University shops. The two methods of construction will be described separately.

In the case of the can constructed by the manufacturing company the can bottom was made up as a separate piece. This bottom unit was then riveted and finally soldered to the fabricated shell forming the sides, as shown in Fig. 12d. The bottom unit was first pressed as indicated in Fig. 12b to form a groove *A* running parallel to the sides and ending in a raised cap *B*. Into the groove *A* was soldered a copper tubing perforated by holes 0.07 in. in diameter as indicated

FIG. 13. ICE FROM NEUTRALIZED CRISFIELD WATER FROZEN IN NEW TYPE OF ICE CAN SHOWN IN FIG. 12

in Fig. 12a, thus forming the bottom air header. Air is supplied to the bottom header by means of a main supply line D, a copper tube connected to the distribution header B, as indicated in the detail shown in Fig. 12c and Fig. 12e, and running up the outside of the can to the top where a flexible connection can readily be made to a central air main.

The objection to this construction lies in the fact that the bottom air header cannot be located at the extreme sides of the can. The difficulty arises from a manufacturing detail. The bottom piece in which the perforated copper air header was soldered was first prepared and was then crimped and riveted to the shell forming the sides. In order to make this latter joint water tight it was in turn soldered,

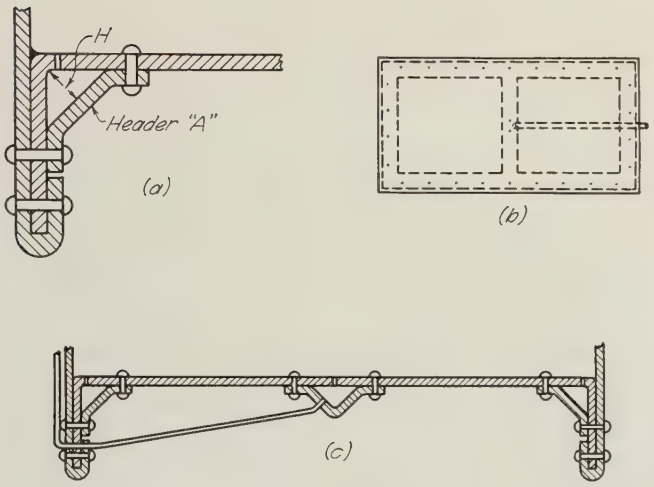

FIG. 14. DETAILS OF NEW TYPE OF ICE CAN FABRICATED IN UNIVERSITY SHOPS

which necessitated reheating the bottom edges. If the perforated header was placed closer to the sides, it was feared that the solder holding it in place would be melted during the reheat. This would not only have loosened the header but would have plugged the small holes with solder.

The result of freezing neutralized Crisfield water in this can is shown in Fig. 13. Agitation was afforded by 1.3 cu. ft. of air per min. for the first two hours, followed by 0.3 cu. ft. per min. for the remainder of the run. The brine temperature was 16 deg. F. Two cores were removed, one of 7.5 gallons, a second of 1 gallon.

The can constructed in the University shops and which more nearly duplicates those conditions existing in the experimental unit shown in Fig. 6 was fabricated as follows: The bottom unit was also crimped, riveted, and soldered to a standard side shell. This accomplished, the bottom air header was formed by riveting, followed by soldering, a pressed piece *A*, into the corners of the bottom as shown in Fig. 14a. The height of the triangular space *H* thus formed was 0.25 in. A more complete view of the air header thus formed is shown in Fig. 14b. The holes leading from the air header into the can which were 0.0635 in. in diameter were drilled before the header was formed. An air supply tube *B*, shown in Fig. 14c, conveyed air to the bottom header. The result of freezing the neutralized Crisfield water in this

FIG. 15. ICE FROM NEUTRALIZED CRISFIELD WATER FROZEN IN TYPE OF ICE CAN SHOWN IN FIG. 14

can is shown in Fig. 15. The ice was produced under the same conditions as that shown in Fig. 13.

Both of the proposed cans would undoubtedly be most effectively operated in the can group type of installation, wherein up to as high as thirty cans are handled as a single unit. In this construction the individual air supply lines for each can are permanently connected to a unit header. When the cans are lowered into the brine tank only one connection to the central air main is necessary to supply air to all cans in the unit. If the central air main were modified to include an adjustable orifice for each unit of cans the change from auxiliary to standard air supply necessitated by the proposed method could be quickly effected. Such an adjustable orifice can be readily made from a standard stop cock the plug of which is drilled to form two holes

of different size at right angles, thus forming two orifices. The holes should be of such dimensions that one would deliver to the unit header a volume of auxiliary air sufficient to agitate the cans equally during the first hours of the freezing period when the auxiliary air is necessary, the other a smaller volume of air sufficient to adequately agitate each can for the remainder of the freezing operation. By means of a flexible hose connection the larger volume of air should be admitted to the cans before they are lowered into the brine. After a sufficient length of time the volume of air could be reduced by turning the plug of the stop cock to the smaller orifice. If the orifice holes were carefully drilled and the pressure on the air main maintained constant the volume of air admitted to each can would be capable of accurate regulation.

10. *Summary.*—

(1) A new type of ice can has been developed which meets the requirements necessitated in freezing water containing high concentrations of dissolved salts under conditions wherein an exceedingly high rate of cooling exists while the first portion of the ice is being produced. It is felt that the new can offers a development whereby the air used for agitation during the freezing process may be most effectively applied.

(2) A freezing procedure has been outlined whereby the new type of can may be most effectively employed in large scale ice production.

(3) Several developments in the freezing technique have been proposed which are not at present incorporated in standard procedure. The most radical departure is included in the proposed removal of large cores. The economic factors involved in this step are more explicitly developed in Appendix B.

(4) Two types of cans embodying the specifications developed in this investigation have been described. One has not as yet been considered from the manufacturing standpoint but has produced satisfactory experimental results. The other has been developed by one of the can manufacturing companies on the basis of submitted specifications and has produced results which are strictly successful from a practical standpoint.

(5) Finally, one point concerning the general application of the proposed method should be emphasized. It has been previously stated that the investigation has been arbitrarily limited to a study of a single type of water, namely, that characterized by a pre-

dominating concentration of sodium bicarbonate. This has been true as far as the actual water sources investigated are concerned. It should be evident, however, that the method described is applicable in the case of all types of water supplies available for ice manufacture. In the work being reported the solutions actually subjected to freezing have been typically sodium sulphate in nature, as indicated by the analysis shown in Table 2. A more concrete example of the general possibilities of this development is, however, found in the results obtained using solutions of sodium chloride as described in Appendix A. It has been shown that when a solution of sodium chloride containing 60 grains per gallon (1020 parts per million or 0.1 per cent by weight) is frozen at a temperature of 16 deg. F. in cans of standard design great difficulty is encountered in preventing the formation of an opaque shell encasing the resulting block of ice even though an extra amount of air is employed. It has been determined, however, that the critical concentration for sodium chloride, beyond which no mechanical agitation is sufficient to prevent opacity, is 253 grains per gallon (4400 parts per million or 0.44 per cent by weight). If mechanical agitation could be improved to a point where opacity would result only when the critical concentration was reached in the core water, it would obviously become possible to greatly increase the range of salt concentration wherein water supplies could be effectively used in artificial ice production. At present a great difference exists between the actual concentration (60 grains per gallon in the case of sodium chloride) beyond which it is now impractical to proceed because of the opacity which results at the sides of the ice block and the so-called critical concentration occasioning opacity in the case of these solutions. In practically no case of naturally occurring water sources does the original salt concentration approach the fundamental critical concentration occasioning opacity. The future course of the problem would, therefore, seem to be indicated in developing efficient and yet economical methods by which solutions being frozen could be so effectively agitated during the first hours of the freezing period that localized salt concentration could be entirely eliminated, the unfrozen core water being maintained continuously homogeneous in the face of high rates of cooling. It is felt that improved design of the ice can developed in the course of this investigation will result in a future development by means of which any water source to be considered as an industrial supply may be effectively utilized in raw water ice production.

III. Chemical Method Applicable in Decreasing Total Dissolved Salts in the Case of Sodium Bicarbonate Waters

11. *Introduction.*—Application of the method previously described would entail the purchase of new freezing equipment in plants already equipped with standard cans since the success of the method essentially depends upon the use of the new type developed during the investigation. The second method was developed in order that sodium bicarbonate waters could be used in the production of a desirable quality of ice in plants already possessing standard freezing equipment. This was accomplished by decreasing the concentration of salts dissolved in the water prior to the freezing operation by means of a new method of water treatment.

At the time the present investigation was undertaken no chemical method of water treatment had been developed whereby concentration of salts in a water of the sodium bicarbonate type could be materially reduced. No relatively insoluble sodium salts exist which are formed as the result of simple chemical reaction. The sodium bicarbonate contained in the water could be converted into sodium sulphate or chloride by neutralization with sulphuric or hydrochloric acids, but in each case the amount of material remaining in solution was practically unchanged. To actually reduce the salt concentration it was necessary to resort to either distillation or to the method of electrical osmosis recently developed by one of the water treating companies. Both were unfortunately characterized by high operative cost.

It is well known, however, that similar types of solutions containing magnesium or calcium bicarbonates in place of sodium can be effectively treated so that the salt concentration is reduced. When calcium hydroxide or lime is added to such solutions chemical reaction results due to the fact that magnesium hydroxide and calcium carbonate, two relatively insoluble compounds, are formed. The reaction is assumed to proceed as follows:

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} + \underset{\text{Calcium hydroxide}}{2Ca(OH)_2} \longrightarrow \underset{\text{Magnesium hydroxide}}{Mg(OH)_2} + \underset{\text{Calcium carbonate}}{2CaCO_3} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} + \underset{\text{Calcium hydroxide}}{Ca(OH)_2} \longrightarrow \underset{\text{Calcium carbonate}}{2CaCO_3} + \underset{\text{Water}}{2H_2O}$$

The approximate solubilities of the substances involved in these reactions are shown in Table 3. The use of calcium hydroxide or lime under these conditions is known as the lime softening process.

It became apparent, therefore, that if by some means the sodium ions existing in a sodium bicarbonate solution could be changed to

TABLE 3

APPROXIMATE SOLUBILITIES OF SALTS INVOLVED IN LIME SOFTENING PROCESS

Salt		Solubility at 70 deg. F. in parts per million
Magnesium bicarbonate	$Mg(HCO_3)_2$	1400
Calcium hydroxide	$Ca(OH)_2$	1700
Magnesium hydroxide	$Mg(OH)_2$	9
Calcium carbonate	$CaCO_3$	13

magnesium or calcium the total concentration of salts dissolved in the solution could be effectively reduced.

On the basis of this speculation, it remained to be determined whether any so-called base-exchange reaction could be effected under the conditions existing in the typical sodium bicarbonate water found at Crisfield, Maryland, which would result in an exchange of sodium for magnesium or calcium ions and whether the water produced on subsequent liming would possess a sufficiently low concentration of dissolved salts to permit the production of marketable ice when the water was frozen under standard operating conditions.

12. *Zeolite Water Softening.*—There is a well known method, involving the use of so-called zeolites, by means of which the basic ions existing in a solution may be exchanged. An application of the method is found in the treatment of domestic water supplies.

The objectionable qualities of such supplies are the dissolved calcium and magnesium salts which they contain. It is these constituents which comprise the so-called "hardness." In the ordinary application of the zeolite method water containing calcium or magnesium ions is passed through a column of the zeolite material. This material is an insoluble porous substance of complex chemical composition a portion of whose reacting surface consists of sodium in a form capable of passing into solution when an equivalent quantity of calcium or magnesium replaces it in the structure of the zeolite. Such exchange is continued until no further efficient exchange of sodium for calcium or magnesium ions takes place. At this point it is assumed that the amount of sodium available for exchange has become so reduced and that the magnesium and calcium zeolites formed have so completely covered the effective exchange surface that further efficient exchange is rendered impossible. To regain its former softening capacity the sodium zeolite must be regenerated. In order to accomplish this the water to be softened is by-passed and the zeolite is washed with a

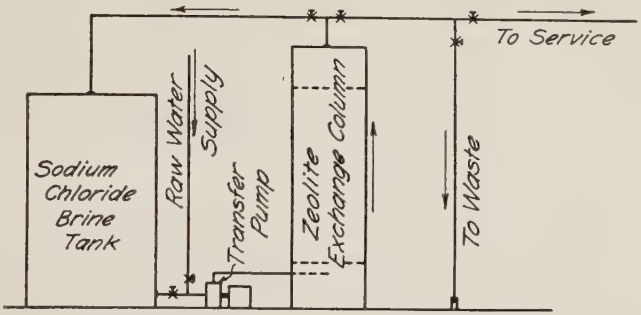

FIG. 16. FLOW SHEET OF COMMERCIAL ZEOLITE WATER SOFTENER

concentrated solution of sodium chloride. Under these conditions the previous operation is reversed. Sodium now enters the zeolite, driving out the calcium and magnesium which was previously removed from the water by the exchange reaction. When a sufficient quantity of the calcium and magnesium is displaced treatment with the concentrated sodium brine is discontinued, the excess sodium chloride solution remaining in the pores of the exchange material is removed by washing, and the zeolite is again capable of exchanging its freshly gained replaceable sodium for calcium or magnesium from solutions containing these latter ions at the relatively low concentrations in which they exist in naturally occurring "hard" waters. A flow sheet of the water softening process is shown in Fig. 16.

It is therefore apparent that the exchange capacity of a zeolite is reversible, the direction in which the exchange predominates being dependent upon the relative concentration of the substances involved in the reaction, both in the solution and in the solid zeolite.

13. *Reversed Zeolite Process.*—In order to clarify the subject an arbitrary classification has been made wherein the various zeolites are designated according to the predominating exchangeable constituent present. Thus, a zeolite in which exchangeable sodium predominates is termed a sodium zeolite, one in which exchangeable magnesium predominates, a magnesium zeolite.

On the basis of the scant experimental data recorded in connection with the general phenomenon of base-exchange reactions, the problem essentially resolved itself into ascertaining whether calcium or magnesium zeolite would effectively exchange its replaceable calcium or magnesium for sodium ions when the latter were present at a concentration equivalent to that existing in the Crisfield water, and further, to what extent this exchange would proceed.

Following a systematic laboratory investigation* it was determined that these zeolites are capable of entering into exchange reactions with solutions containing sodium bicarbonate wherein the concentration of this salt is comparable to that found in the Crisfield water. Furthermore, it was determined that magnesium zeolite possesses properties which render it the more desirable of the two.

A decided attempt was made to utilize calcium zeolite due to the fact that calcium chloride, which would then be used as the regenerating solution, could be obtained at a lower cost than the corresponding magnesium salt. The use of calcium zeolite was, however, finally determined to be impractical even though the efficiency of the exchange effected was acceptable. In all sodium bicarbonate solutions there exists an equilibrium between bicarbonate, carbonate, and hydroxyl ions, the relative concentrations of bicarbonate and carbonate ions depending upon the hydroxyl ion concentration or alkalinity of the solution. In the Crisfield water the alkalinity is such† that a sufficient concentration of the carbonate ions exists to cause calcium carbonate, formed as the result of exchange, to precipitate from solution. It became evident that such precipitation occurring at the surface of the zeolite was sufficient to render in time the zeolite incapable of further exchange.

In the case of the magnesium zeolite, however, no possible precipitate formation exists under conditions encountered in any naturally occurring sodium bicarbonate water. The most insoluble compound of magnesium capable of being formed under these conditions is magnesium hydroxide. This compound according to Buswell and Greenfield‡ is not precipitated until the alkalinity§ is much greater than that naturally occurring in this type of solution. Magnesium zeolite is therefore not only admirably adapted to the specific conditions prevailing in sodium bicarbonate solutions but has been shown in addition to possess both a higher exchange efficiency and higher exchange capacity for sodium ions than calcium zeolite.

For general commercial use there are three distinct types of zeolites available: (1) the natural-occurring greensand (glauconite), (2) an artificial material prepared by fusing kaolin, quartz, and sodium carbonate, and (3) the artificially-prepared substance manufactured by

*For details of the complete laboratory investigation and subsequent semi-plant scale operations see Appendix C.

†The pH of the solution is approximately 8.4.

‡The Illinois State Water Survey, Bulletin No. 22, 1928.

§Under the conditions existing in any natural bicarbonate type solution the pH must be increased to 9.5-10, before magnesium hydroxide will form. This point is graphically indicated in Fig. 39, Appendix C.

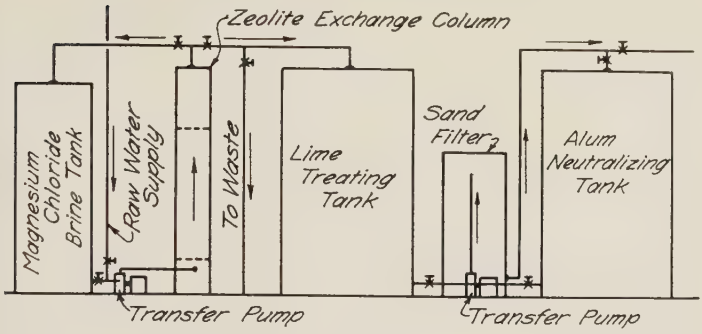

Fig. 17. Flow Sheet of Reversed Zeolite Process

mutually precipitating sodium aluminate and sodium silicate. Commercial samples of each type were obtained and studied in experimental laboratory runs. It was determined that all three types could be utilized in the exchange reactions considered, although the efficiency of exchange varied among the different types. In all laboratory and semi-plant-scale operations undertaken the synthetic material of type 3 was used. Further investigation will undoubtedly indicate, however, that under specific operating conditions each of the three types will develop the same degree of application that it now holds in the field of water softening.

By using magnesium zeolite in the treatment of sodium bicarbonate solutions the process of water softening is essentially reversed. Starting with commercial sodium zeolite the magnesium compound is prepared by washing the exchange material with a magnesium chloride brine. The sodium in the zeolite is thereby replaced by magnesium. To remove the excess brine held by the porous material washing is effected by means of the raw water. When the last trace of magnesium chloride has been removed the effluent solution is recovered, treated by means of lime and filtered. The filtered solution after being neutralized by means of sulphuric acid or aluminum sulphate is then frozen. A flow sheet of the reversed zeolite process is shown in Fig. 17.

The method finally utilized in the case of both laboratory and plant scale operation is as follows: Commercial sodium zeolite, the material commonly used for water softening, is placed in a vertical container through which can be passed either the water to be treated or the regenerating brine. A 3-per-cent solution of magnesium chloride is then forced through the zeolite bed, thus effecting exchange between

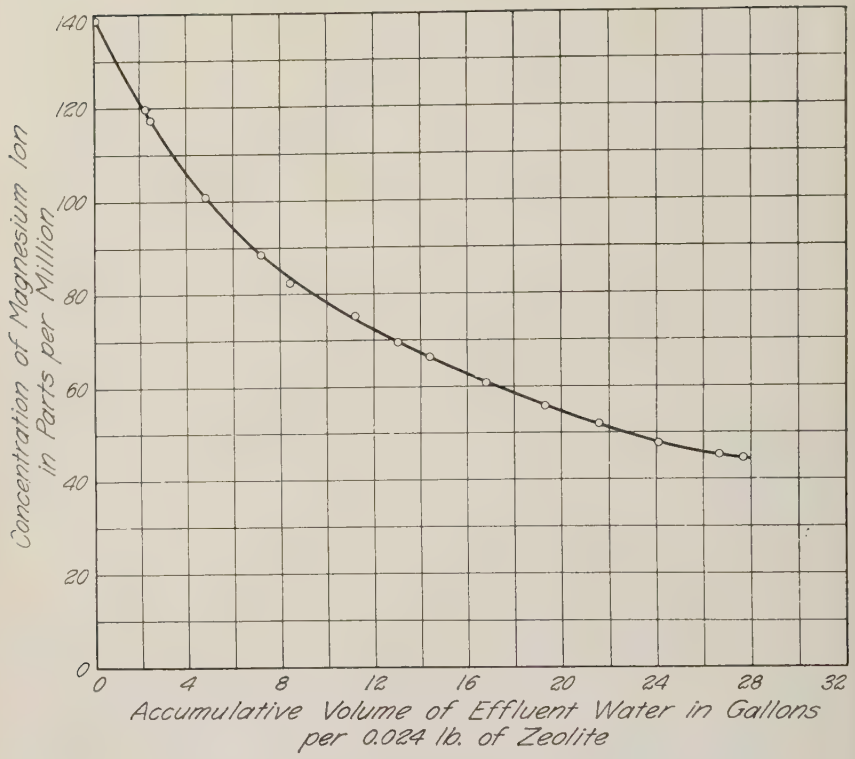

FIG. 18. EXCHANGE DATA FOR MAGNESIUM ZEOLITE AND SODIUM BICARBONATE SOLUTION

the magnesium ions in the brine and the sodium in the zeolite. Since the exchange is at all times proportional to (1) the ratio

$$\frac{\text{magnesium ion concentration}}{\text{sodium ion concentration}}$$

in the solution and (2) the ratio

$$\frac{\text{concentration of replaceable sodium}}{\text{concentration of replaceable magnesium}}$$

in the zeolite it is evident that the rate at which the magnesium zeolite will be formed is at first exceedingly great and then progressively decreases. Since the exchange of sodium for magnesium takes place in the ratio of their equivalent weights, the concentration of sodium ion in the effluent brine is at all times a measure of the degree to which magnesium zeolite is being formed. When it becomes evident that the replaceable metal in the zeolite is practically all magnesium,

TABLE 4

COMPOSITION OF CRISFIELD WATER COMPLETELY TREATED WITH MAGNESIUM ZEOLITE

Hypothetical Combinations		Concentration, parts per million
Magnesium bicarbonate	$Mg(HCO_3)_2$	644
Sodium chloride	NaCl	94
Sodium sulphate	Na_2SO_4	77
Aluminum oxide	Al_2O_3	1
Silica	SiO_2	12
Total Solids		828

the first cycle in the treatment, to be subsequently called the regeneration cycle, is complete.

At this point there remains held in the pores of the zeolitic material a large amount of unbound magnesium chloride which must be completely removed by washing before the effluent water can be collected for lime softening. In the washing cycle, therefore, the raw water available is passed rapidly through the zeolite bed until the unbound magnesium chloride has been completely removed by displacement. The course of the washing cycle is followed by determining the concentration of chloride ion in the effluent solution. When the concentration of this constituent reaches a value equal to its concentration in the raw water the washing cycle is complete. At this point the greatest exchange of sodium ion for magnesium takes place. As the raw water continues to be passed through the column, however, the amount of exchange progressively decreases, since the available magnesium zeolite becomes progressively depleted. A typical exchange curve, wherein the average concentration of magnesium ion resulting in the effluent solution is plotted against the volume of solution recovered, is shown in Fig. 18.

When the average concentration of magnesium ion in the treated water is sufficient to result in the desired reduction of dissolved salts upon subsequent lime treatment the exchange cycle is stopped. The zeolite column, consisting largely of sodium zeolite, is then washed with magnesium chloride to regenerate the magnesium compound. After being washed the column is again ready for the next exchange cycle.

14. *Amount of Exchange Required.*—To obtain the greatest reduction of dissolved salts the magnesium zeolite reaction must be continued until the concentration of magnesium ion in the effluent

Table 5

Composition of Crisfield Water after Complete Treatment with Magnesium Zeolite followed by Lime Softening

Hypothetical Combinations		Concentration, parts per million
Calcium carbonate	$CaCO_3$	10
Magnesium hydroxide	$MgOH$	3
Sodium chloride	$NaCl$	94
Sodium sulphate	Na_2SO_4	77
Aluminum oxide	Al_2O_3	1
Silica	SiO_2	12
Total Solids		197

solution is equivalent to the sodium originally present in the raw water as carbonate or bicarbonate. In the case of the typical water found at Crisfield the concentration of sodium bicarbonate is 741 parts per million. From this there results a sodium ion concentration of 203 parts per million. The equivalent concentration of magnesium ion is 106 parts per million. According to Fig. 18, 0.024 cu. ft. of magnesium zeolite will produce 4.0 gallons of effluent solution having an average magnesium concentration of 106 parts per million. The Crisfield water thus treated has the composition shown in Table 4. Applying lime treatment as practiced in efficient water treating plants,* the concentration of magnesium ion resulting from residual magnesium hydroxide would be 1.4 parts per million, the final concentration of calcium ion from residual calcium carbonate 4 parts per million. The lime-treated water would then have the composition shown in Table 5. Such treatment results in a decrease of the total solids from 949 to 197 parts per million, a decrease of 752 parts per million, or 79 per cent.

To determine the effectiveness of this reduction in total solids, a synthetic solution was prepared by dissolving in distilled water the necessary chemicals to form a solution having the composition shown in Table 5. This solution was then frozen in a standard 400-lb. can at 15 deg. F. The amount of air used for agitation was 0.12 cu. ft. per min. applied through a standard side drop tube. The resulting cake of ice, from which no core solution was removed, is shown in Fig. 19.

In order to check this performance, actual Crisfield water was treated in a semi-plant-scale installation.† Numerous runs were made

*See Appendix D for conditions existing as the result of efficient lime treatment.
†For details see Appendix D.

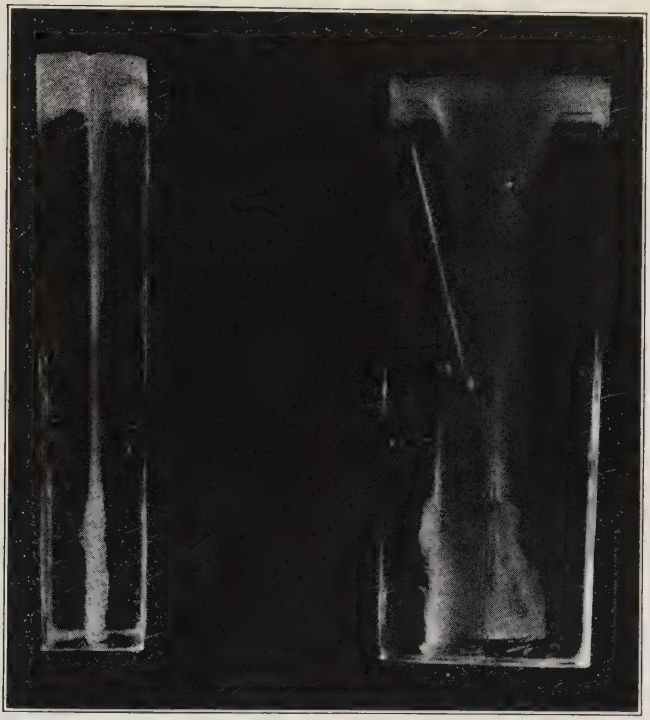

FIG. 19. ICE FROM SYNTHETIC SOLUTION CORRESPONDING TO CRISFIELD WATER WITH DISSOLVED SALTS REDUCED 79 PER CENT

The reduction to be effected by magnesium zeolite followed by lime softening.

in which the volume of solution treated was in each case approximately 100 gallons, this being sufficient for the freezing of duplicate samples in standard 400-lb. ice cans. The treated solutions were frozen at brine temperatures of 15 deg. F., air agitation being afforded by 0.12 cu. ft. of air per min. applied to standard side drop tubes. The resulting ice was strictly comparable to that shown in Fig. 19.

An examination of the exchange data shown in Fig. 18 leads to the conclusion that the exchange cycle would increase in efficiency if the final concentration of magnesium were allowed to become less than equivalent to the total bicarbonate ion concentration. Under these conditions more solution could be passed through the exchange material per pound of zeolite before regeneration became necessary. In this case the concentration of dissolved salts would be reduced by an amount less than that equivalent to the entire concentration of sodium bicarbonate originally present. An attempt was therefore made to

TABLE 6

COMPOSITION OF SOLUTIONS RESULTING FROM VARIOUS DEGREES OF MAGNESIUM ZEOLITE TREATMENT

Hypothetical Combinations		Composition, parts per million	
		Case (1)	Case (2)
Magnesium bicarbonate	$Mg(HCO_3)_2$	540	402
Sodium bicarbonate	$NaHCO_3$	119	278
Sodium chloride	NaCl	94	94
Sodium sulphate	Na_2SO_4	77	77
Aluminum oxide	Al_2O_3	1	1
Silica	SiO_2	12	12

TABLE 7

COMPOSITION OF NEUTRALIZED SOLUTIONS RESULTING FROM VARIOUS DEGREES OF MAGNESIUM ZEOLITE TREATMENT

Hypothetical Combinations		Concentration, parts per million	
		Case (1)	Case (2)
Calcium sulphate	$CaSO_4$	14	14
Magnesium sulphate	$MgSO_4$	7	7
Sodium sulphate	Na_2SO_4	177	312
Sodium chloride	NaCl	94	94
Aluminum oxide	Al_2O_3	1	1
Silica	SiO_2	12	12
Total Solids		305	440

determine the minimum reduction of dissolved salts which would still render the production of marketable ice possible in standard equipment.

Two hypothetical cases were considered, one in which the exchange is continued until the average concentration of magnesium ion in the treated water is 89 parts per million, the other until it becomes 67 parts per million. Referring to Fig. 18 it is seen that in the first case the volume of effluent solution resulting from 0.024 cu. ft. of zeolite is 7.2 gallons, while in the second the volume of recovered solution is 14 gallons. The resulting chemical composition of cases (1) and (2) is that shown in Table 6.

When the solutions shown in Table 6 are treated with calcium hydroxide the residual concentration of calcium and magnesium is that shown in Table 5. During the lime treatment the unconverted sodium

FIG. 20. ICE FROM CRISFIELD WATER WITH DISSOLVED SALTS REDUCED 68 PER CENT

The reduction was effected by means of magnesium zeolite followed by lime softening and conversion of residual carbonate to sulphate. The ice was frozen in a standard 400-lb. can using standard air for agitation.

bicarbonate is changed to sodium carbonate. Since it was determined during the investigation that sodium carbonate is more effective in producing opaqueness than an equivalent concentration of sodium sulphate it was additionally assumed that as a subsequent step in the treatment of these two samples the resulting carbonate is neutralized with either sulphuric acid or aluminum sulphate, thus forming the corresponding sulphates of sodium and calcium. The composition of the resulting solutions is that shown in Table 7. Case (1) represents a decrease in total solids of 644 parts per million, or 68 per cent, Case

FIG. 21. ICE FROM CRISFIELD WATER WITH DISSOLVED SALTS REDUCED 54 PER CENT

The reduction was affected by means of magnesium zeolite followed by lime softening and conversion of residual carbonate to sulphate. The ice was frozen in a standard 400-lb. can using standard air for agitation.

(2) a decrease in total solids of 509 parts per million, or 54 per cent. The result of freezing synthetic solutions having the compositions indicated in Table 7 under standard operating conditions in standard 400-lb. cans is shown in Figs. 20 and 21, respectively. No core water was removed in either case. The temperature at which both samples were frozen was 14 deg. F. The amount of air used for agitation was 0.12 cu. ft. per min. per can. In the case of both samples the removal of cores would have resulted in the production of distinctly marketable ice. It is obvious, however, that the tendency to form a white veil

TABLE 8

COMPOSITION OF CRISFIELD WATER TREATED WITH MAGNESIUM ZEOLITE UNTIL LIME SOFTENING WILL PRODUCE 30-PER-CENT REDUCTION IN DISSOLVED SALTS

Lime treatment followed by neutralization to sulphate

Hypothetical Combinations		Concentration, parts per million
Calcium sulphate	$CaSO_4$	14
Magnesium sulphate	$MgSO_4$	7
Sodium sulphate	Na_2SO_4	508
Sodium chloride	NaCl	94
Aluminum Oxide	Al_2O_3	1
Silica	SiO_2	12
Total Solids		636

has made its appearance, and that greater agitation, especially at the sides of the can, must be effected in order to prevent the formation of the undesirable white shell if the utilization of higher concentrations of dissolved salts is to be attempted.

Data have been presented in Chapter II, however, which demonstrate conclusively that solutions resulting from the neutralization of the Crisfield water wherein no decrease in dissolved salts is effected may be used to produce a marketable grade of ice if sufficient auxiliary air is employed for agitation during the first hours of the freezing operation. It, therefore, became obvious that lower concentrations of magnesium in the effluent solutions than that indicated in Case (2), Table 6, would undoubtedly yield solutions which could be effectively frozen in standard cans if auxiliary air were used during the initial freezing period.

Numerous runs were subsequently made, using semi-plant-scale equipment, wherein the exchange with magnesium zeolite was continued until the average concentration of magnesium in the effluent water was 33 parts per million, corresponding to 231 parts per million of sodium bicarbonate. After lime treatment followed by neutralization of the carbonate to sulphate the concentration of salts dissolved in the solution was that shown in Table 8. Such treatment resulted in a decrease in dissolved salts of 313 parts per million, or 33 per cent. The result of freezing such solutions in standard 400-lb. ice cans at brine temperature averaging 14 deg. F. is shown in Fig. 22. Agitation was afforded by 1.3 cu. ft. of free air admitted through a side drop tube of the type shown in Fig. 4a for 2 hours, the air supply then being reduced to 0.3 cu. ft. per minute for the remainder of the run.

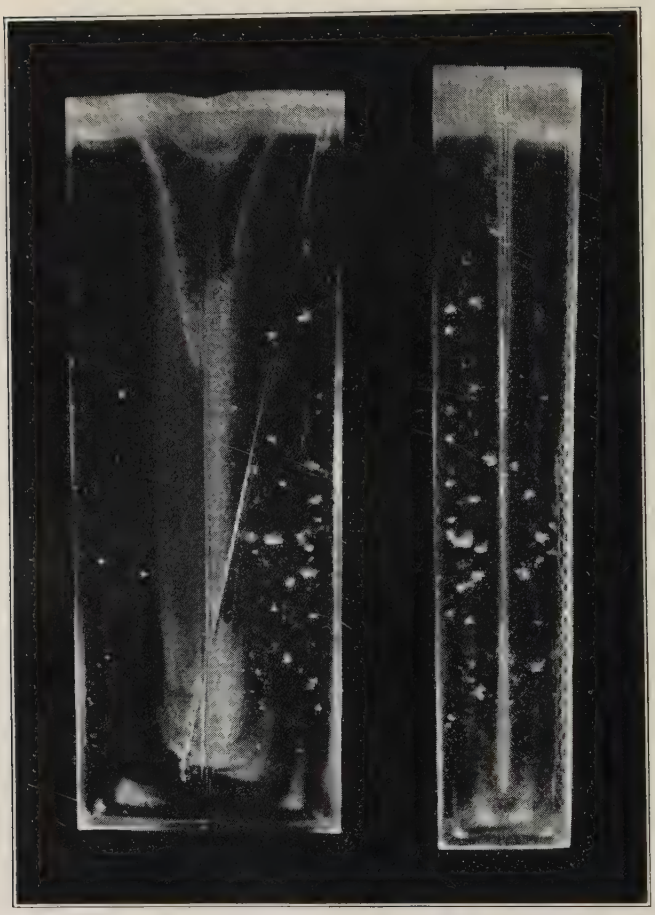

FIG. 22. ICE FROM CRISFIELD WATER WITH DISSOLVED SALTS REDUCED 33 PER CENT

The reduction was affected by means of magnesium zeolite followed by lime softening and the conversion of residual carbonate to sulphate. The ice was frozen in a standard 400-lb. can using an auxiliary air supply for agitation. A large core was also removed.

Air agitation was invariably started before the can was placed in the brine. Two cores were removed in each case, one of 10 gallons, followed later by a second of 2 gallons.

That the salt concentration may not be increased appreciably above 636 parts per million before more efficient air agitation than can be obtained using standard equipment becomes necessary was demonstrated when the neutralized Crisfield water was frozen in a standard 400-lb. can agitated by means of auxiliary air during the initial freezing period. The brine temperature was 16 deg. F., and a

FIG. 23. ICE FROM NEUTRALIZED CRISFIELD WATER WITH CONCENTRATION OF DISSOLVED SALTS 831 PARTS PER MILLION

The ice was frozen in a standard 400-lb. can using an auxiliary air supply for agitation. A large core was also removed.

10- followed by a 1-gallon core was removed. The result is shown in Fig. 23.

15. *Summary.*—

(1) Utilizing the exchange properties of magnesium zeolite followed by liming and subsequent neutralization by means of either sulphuric acid or aluminum sulphate, sodium bicarbonate water

supplies can be successfully rendered available for the production of marketable raw water ice when use is made of standard freezing equipment.

(2) If a sufficient amount of the salt originally dissolved in the water is removed by means of this procedure, standard cans and standard air agitation suffice to produce a thoroughly marketable product.

(3) If a relatively small amount of the salts originally dissolved in the water is removed marketable ice can be produced in standard cans if auxiliary air agitation is provided during the first hours of the freezing operation and if comparatively large cores are removed.

Appendix A

Conditions Occasioning Formation of Opaque Ice

1. *Introduction.*—Since ice manufactured in electrified plants must be produced from natural water supplies which invariably contain dissolved salts, and yet must possess a high degree of transparency, the effect of the dissolved constituents of the water being frozen upon the appearance of the product is of great importance. Existing data upon this point are unfortunately incomplete. In the course of this investigation, however, a working hypothesis has been developed which, while not held to be a complete statement, is felt to account for many of the phenomena encountered, and to possess possibilities in directing further research.

2. *General Discussion.*—The conditions accompanying the cooling of any aqueous salt solution may best be examined by considering an empirical system composed of two components A and B, the temperature—composition diagram of which is shown in Fig. 24.

As pure liquid A is cooled, a solid phase appears when the temperature reaches the freezing point E of the pure substance at which all of the liquid sharply solidifies. When, however, a solution of B in A having the composition x is cooled, no solid appears at E, and the temperature must be lowered to Z before any solid formation occurs. The presence of the second component B is thus seen to depress the freezing point of A.

The composition of the solid appearing at Z is, however, considered to be pure A. Since separation of solid A concentrates the solution with regard to B, further separation of A can be produced only by lowering the temperature of the solution along the line E-F. In the case of pure B or of mixtures of A in B a similar condition exists. At the temperature G pure liquid B solidifies. Along the line F-G solutions of A in B exhibit the separation of pure B. At F, where the two lines E-F and F-G coincide, the solid separating is a mixture of A and B, the eutectic. Consequently, if the original concentration of the solution is such that either solid A or solid B separates when the solution is sufficiently cooled, continued removal of heat causes further separation of A or B until the eutectic temperature is reached, when the eutectic mixture separates. If at this point heat continues to be removed from the system all of the solution remaining unfrozen will completely solidify as the eutectic mixture.

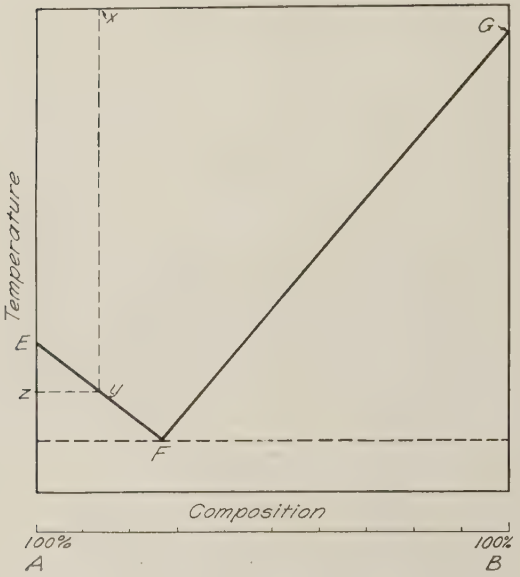

FIG. 24. TEMPERATURE—COMPOSITION DIAGRAM FOR A TWO COMPONENT SYSTEM

It is obvious, therefore, that as any aqueous solution is cooled a solid phase finally appears which is either solid ice, solid salt, or a mixture of ice and salt, the eutectic.

3. *Freezing of Industrial Water Supplies.*—In the case of actual water supplies the system invariably consists of a number of dissolved constituents and the conditions prevailing in the two component systems discussed do not strictly hold. The conclusions previously reached are sufficiently broad, however, to apply generally in the case of all solutions to be encountered.

Since the quality most desired in manufactured ice is transparency, a physical condition wherein light entering the ice cake is neither materially refracted nor absorbed, it is extremely probable that the separation of the eutectic mixture would produce the opposite of transparency, opaqueness, due to the optical heterogeneity occasioned by the mutual precipitation of two optically dissimilar substances. Therefore, any water source to be used in ice production should be characterized by the separation of ice alone when the solution is cooled. If solid salt should first separate, followed by the subsequent separation of the eutectic, opacity would result for the same cause.

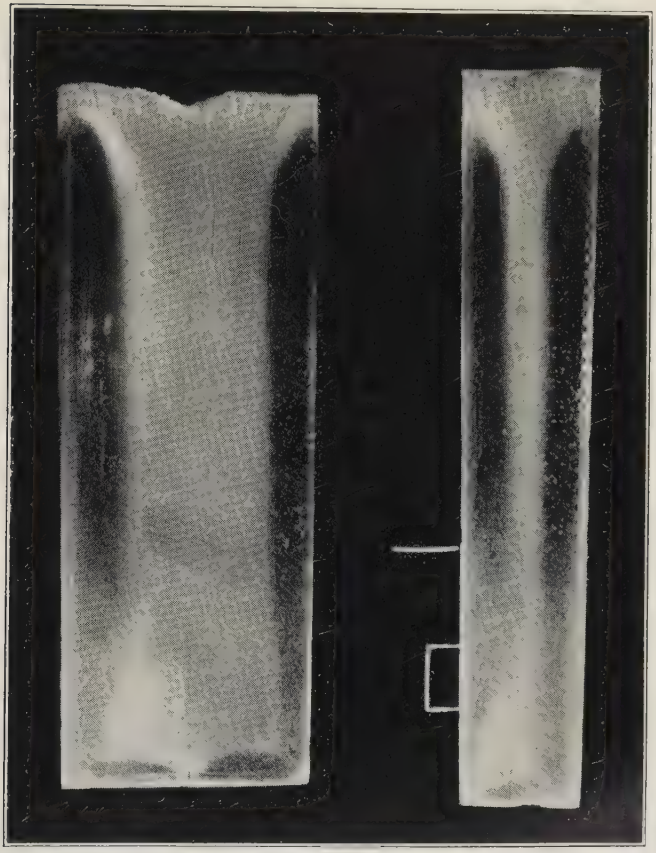

FIG. 25. ICE PRODUCED ON FREEZING A 0.1-PER-CENT SODIUM CHLORIDE SOLUTION AT 16 DEG. F.

Some doubt exists, however, as to whether the separation of an eutectic mixture invariably produces opacity. Unquestionably opacity results if the salt concentration in the eutectic is sufficiently high. On the other hand, an example of a transparent solid phase being produced under conditions permitting only eutectic formation is found in the case of solutions resulting from lime treatment. Such solutions are saturated with either calcium carbonate or magnesium hydroxide, or both. Since the solubilities of both salts increase as the temperature is lowered* the solid phase separating on cooling is ice, followed eventually, however, by the eutectic mixture of ice and calcium car-

*Johnston and Williamson, Jour. Am. Chem. Soc. 38, 980 (1916). Kline, Jour. Am. Chem. Soc. 51, 2097 (1929).

FIG. 26. TRANSITION BETWEEN TRANSPARENT AND OPAQUE ICE

bonate or magnesium hydroxide. The concentration of these salts in the eutectic, while not accurately known, is unquestionably low. Since practically all waters used in the production of manufactured ice are first treated by means of lime, it is obvious from the amount of transparent ice produced under these conditions that the concentration of salt separating in these specific eutectics is not sufficient to produce

FIG. 27. OUTLINE OF TRANSPARENT ICE CRYSTALS

optical heterogeneity.* Whether higher salt concentrations in the eutectic occasion opaqueness is difficult to determine due to the fact that long before eutectic formation occurs a condition develops in the

*In the case of inefficiently operated lime softening installations a large amount of residual calcium carbonate and magnesium hydroxide invariably results in the effluent water in either a colloidal condition or in a state of suspension. Cooling of such solutions eventually causes precipitation of the material thus held, in a fine state of division. Becoming entrapped in the ice face this material subsequently occasions opacity. This particular difficulty may be remedied either by removing the material from solution by means of efficient flocculating agents or by converting it into a more soluble form by means of subsequent neutralization. Opacity resulting in this case should not be mistaken for evidence that the eutectic mixture containing calcium carbonate and magnesium hydroxide is necessarily opaque.

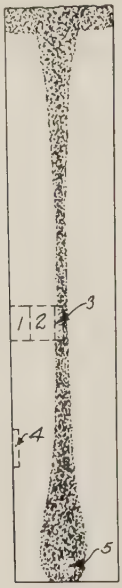

FIG. 28. METHOD OF SAMPLING ICE CAKE SHOWN IN FIG. 25

unfrozen solution which is undoubtedly the predominating factor in the production of opaque ice.

4. *Influence of Solution Environment on Crystal Habit—The Case of Sodium Chloride Solutions.*—The conditions prevailing on cooling solutions of sodium chloride are the same as those generally outlined in Section 2. The eutectic temperature in this case is –6.20 deg. F., the eutectic composition 22.43 per cent of salt by weight. If solutions of sodium chloride containing less than 22.43 per cent of salt are cooled under conditions existing in standard ice plants, wherein the average brine temperature is 16 deg. F., 22.2 deg. F. above the eutectic temperature, it is obvious that the only solid phase capable of being formed is ice. Yet, when a solution containing 0.1 per cent of sodium chloride (1020 parts per million) was frozen at 16 deg. F. in a standard 400-lb. can using 1.3 cu. ft. of air for agitation (approximately four times that used in standard practice), the product was that shown in Fig. 25. Marked opaqueness resulted even though the solid phase seemingly consisted of the single component ice.

Some idea of the sharp transition between the formation of the transparent and the opaque ice is shown in Figs. 26 and 27. The transparent ice was characterized by large well-oriented crystals

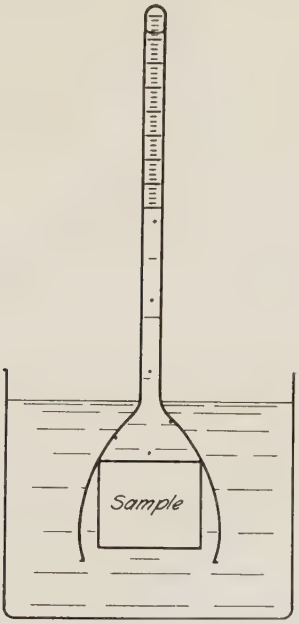

FIG. 29. APPARATUS FOR DETERMINING ENTRAINED AIR

formed perpendicular to the sides of the container. The outlines of these crystals, which in the accompanying illustration give some idea of their actual size, are shown in Fig. 27. The opaque ice, on the other hand, was characterized by relatively small, unoriented crystals. Whereas the transparent ice was extremely homogeneous and possessed many of the characteristics of a single large crystal, the opaque ice was composed of a mass of small individual particles held loosely together.

Since the opaque ice resulted under conditions wherein the solution being frozen was saturated with air used for agitation, the presence of air was considered as a possible contributing factor in the production of opacity. In order to investigate this point and to obtain data concerning the distribution of sodium chloride throughout the frozen ice cake, the block of ice shown in Fig. 25 was sampled at the points indicated, the method of sampling being graphically shown in Fig. 28. Each sample was subsequently analyzed for sodium chloride and entrained air. For this purpose the samples were divided into two portions. One was melted, the concentration of chloride ion determined in the recovered solution becoming a measure of the amount of sodium

Table 9

Distribution of Sodium Chloride and Entrained Air

Sample Number	Character of ice sample	Sodium Chloride, parts per million	Entrained air, cc./kilogram
1	Opaque at surface, largely clear	8	0
2	Clear	10	0
3	Opaque	1650	5
4	Opaque at surface, largely clear	54	3
5	Opaque	362	26
Original Solution		1050	

chloride present. Since on the basis of formal phase-rule consideration the composition of the solid phase has been limited to pure solid water the sodium chloride can only be assumed to be present in solution, and therefore dissolved in the mother liquor entrained between the ice crystals. That a second possibility exists will be presented later.

The concentration of entrained air was determined by placing the second portion of the solid ice sample in a water bath previously saturated with air and containing a modified eudiometer tube. The complete arrangement is shown in Fig. 29. The ice on melting liberated any entrained air, the air being in turn measured in the graduated tube. The results of a typical series of these determinations are shown in Table 9, the sample numbers referring to Fig. 28.

An examination of Table 9 indicates that of the two the presence of salt is by far the greater factor in the production of opacity. Distinct opacity resulted at the sides of the cake due to the rapid cooling resulting when the can was first placed in the cold brine. An analysis of the ice formed during this initial period distinctly indicates the presence of sodium chloride and the complete absence of air. Since air must of necessity be held by entrainment alone, the conditions in effect during the initial stages of the freezing operation would be expected to favor the production of opacity from this source. The absence of entrained air at this point leads to the conclusion that it is of only secondary importance. In fact it is recognized as a matter of experience that increasing the volume of air used during the initial stages of the freezing operation is one of the most effective methods available for the prevention of opacity. The occurrence of the large volume of entrained air in samples (3) and (5), and principally in (5), is to be anticipated due to the fact that as the final solution freezes

it is whipped into a foam by the air used for agitation, resulting in the occurrence of a large amount of entrained air at this point.

The principal conclusion to be drawn from the results shown in Table 9 is that the occurrence of opacity is primarily associated with the presence of the salt dissolved in the solution from which the ice is formed.

The hypothesis developed to account for this phenomenon essentially assumes that the salt dissolved in the unfrozen solution finally becomes sufficiently concentrated to alter definitely and sharply the crystal size and orientation of the ice subsequently formed, thus occasioning opacity due to the optical heterogeneity produced. The factors assumed to occasion this condition are those generally involved in the formation of any new solid phase.

Any sufficiently dilute solution on being cooled finally presents a solid phase, ice. The previously homogeneous system, the solution, is at once transformed to one characterized by phase heterogeneity. The solid phase exists in equilibrium with a solution containing molecular aggregates and ions of the solvent, identical to those comprising its own structure, and likewise with molecular aggregates and ions resulting from the dissolved solute. As a solid phase it exerts a relative attraction for all the constituents with which it is in equilibrium. As the solution is progressively cooled the original ice crystal continues to grow through separation from the solution of similar molecular aggregates of solvent molecules. If, however, continued crystal growth is assumed to result from absorption of molecular aggregates of the solvent due to the attraction of residual valence charges or force fields existing at the crystal interface as has been variously proposed,* it is to be anticipated that such growth would also be accompanied by some degree of adsorption of solute constituents.

A comprehensive summary of the forces in effect at the interface between a crystal and the solution with which it is in equilibrium is found in the following statement by Eckert and France.†

"Niggli,‡ Valeton§ and others have represented the outer zone of a crystal as unsaturated with respect to valence or force fields. The crystal face attempts, therefore, in a suitable environment to reach

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*Mare and Wenk, Z. physik. Chem. vol. 67, p. 470, 1909; vol. 68, p. 104, 1909; vol. 73, p. 685, 1910.
Freundlich, Kapillar. Chemie, 2nd Ed., Leipzig, 1922, pp. 448 et seq., Z. physik. Chem. vol. 75, p. 245, 1910.
Eckert and France, Jour. Am. Ceram. Soc. vol. 10, p. 579, 1927.
Keenan and France, Jour. Am. Ceram. Soc. vol. 10, p. 821, 1927.
Bennett and France, Jour. Am. Ceram. Soc. vol. 11, p. 571, 1928.
†Jour. Am. Ceram. Soc. vol. 10, p. 559, 1927.
‡Z. anorg. allgem. Chem., vol. 110, p. 55, 1920.
§Z. Krist, vol. 59, p. 155, 335, 1924.

an equilibrium by the addition of new particles. Neutralization of forces is, however, not attained, for a new surface forms and growth continues. Crystals can, therefore, be considered as the stable form resulting from the attractive and repulsive anisotropic forces existing in the medium from which growth takes place.

"That crystals are the result of a complicated chemical field existing between the crystal and its environment is evident from the fact that slight amounts of foreign materials in the solution change the shape and form of the crystals remarkably. The effect of urea upon sodium chloride has already been mentioned,* and of no less importance is the effect of gelatin and the dyes mentioned† upon the crystal habit of copper sulphate.

"According to the molecular orientation theory of adsorption as developed by Langmuir and by Harkins, various degrees of adsorption may take place, depending upon the nature of the adsorbed material, adsorbing surfaces and environmental conditions."

The assumption of solute adsorption introduces an obvious contradiction to the conclusions previously reached in Section 2 as the result of formal phase-rule considerations. It was previously stated that in the case of dilute aqueous solutions the only stable solid phase existing above the eutectic temperature was pure solid water or ice. The adsorption hypothesis, however, presupposes relative separation of both water aggregates and salt molecules or ions at the solid interface at all temperatures. The difficulty results from no real disagreement between the two conceptions, but rather from an incomplete statement concerning the application of the phase rule to generalized conditions accompanying heterogeneous equilibrium.

Essentially what was previously stated concerning any two-component system was that at any temperature above the eutectic temperature the solid phase separating is either pure A or pure B. For most practical considerations this assumption is sufficiently correct. Rivett,‡ among others, has pointed out, however, that in any two-component system wherein two phases exist in equilibrium, each component must be distributed to some extent between each phase. The distribution coefficient of each component between the phases may vary in magnitude over a wide range from system to system. In fact, the distribution coefficient is in many cases of such insignifi-

*Korbs, Z. Krist. 43, 450 (1917).
†Quinoline yellow
Ponceau 2 R
Napthol yellow
Methyl violet
Bismark brown
Methylene blue
‡The Phase Rule and the Study of Heterogeneous Equilibria, Milford, London, 1923.

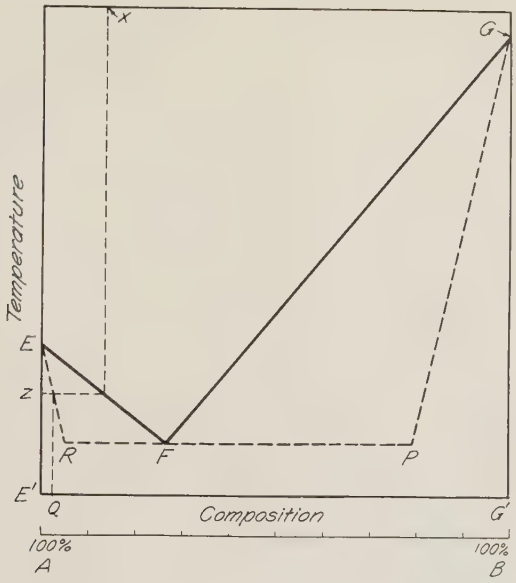

FIG. 30. TEMPERATURE—COMPOSITION DIAGRAM FOR A TWO COMPONENT SYSTEM

cant proportions that the system may formally be considered to be strictly eutectiferous, the solid phase separating from solution being considered to be one or the other of the pure components. However, from a purely theoretical standpoint, whenever a solvent crystallizes from a solution it must always be accompanied by a definite though small amount of the solute.

Graphically this means that the general case previously presented in Section 2 is more exactly represented in Fig. 30. When a solution of A and B having the composition represented by *X* is cooled, a solid phase will appear as before when the temperature *Z* is reached. The composition of the solid phase will not, however, be that of pure A but will consist of a mixture of A and B having the composition Q. The slope of the lines *E-R* and *G-P*, which in turn depend upon the distribution coefficients of B in A and A in B, have been purposely exaggerated in Fig. 30. Actually, they may lie so close to the lines *E-E'* and *G-G'* that, as previously stated, the solid phase for practical purposes may be considered to be the pure component A or B. This distribution, however, is seemingly of sufficient magnitude to effect materially the growth and form of crystals formed from the solution even in those cases where the concentration of solute in the solution is exceedingly small.

FIG. 31. ICE PRODUCED ON FREEZING A 0.4-PER-CENT SODIUM CHLORIDE SOLUTION AT 16 DEG. F.

Thus, in the case of the dilute aqueous solutions used in the production of manufactured ice the solid phase separating may still be considered from a formal standpoint to consist of pure ice. The solid phase should, however, be more accurately considered as a solid solution of solute in ice, the mechanism of its formation being that of adsorption. Since such adsorption generally increases as the solute component becomes concentrated, it is conceivable that with continued separation of ice a point is finally reached at which further concentration of the mother liquor occasions such a sharp disfigurement of the crystal form that opacity results due to the optical heterogeneity produced.

On the basis of this hypothesis there should exist for each solution a definite concentration of dissolved salt or salts in the unfrozen solution, further separation of ice from which results in the formation of an opaque solid phase. When the initial rate of cooling in standard ice

FIG. 32. ICE PRODUCED ON FREEZING A 0.1-PER-CENT SODIUM CHLORIDE SOLUTION SHOWING EFFECT OF SOLUTION CONCENTRATION ON CRYSTAL HABIT

cans is high the concentration of dissolved salts tends to reach this critical concentration locally, resulting in the formation of an opaque veil. No amount of agitation should, however, be successful in preventing opaque ice formation when the homogeneous core water becomes concentrated to the point where the critical concentration is reached. When the 0.1-per-cent sodium chloride solution was frozen

FIG. 33 ICE PRODUCED ON FREEZING A 0.4-PER-CENT SODIUM CHLORIDE SOLUTION SHOWING EFFECT OF SOLUTION CONCENTRATION ON CRYSTAL HABIT

opacity resulted in the core when the concentration of sodium chloride was 0.44 per cent (4400 parts per million). If this represents a critical concentration specific for sodium chloride, solutions possessing a corresponding initial concentration should invariably produce opaque ice irrespective of agitation. To check the validity of the assumption,

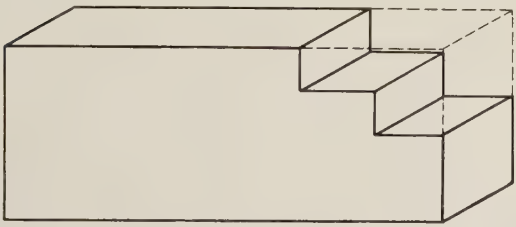

FIG. 34. METHOD OF CUTTING ICE CAKE TO OBTAIN VIEWS SHOWN IN FIGS. 32 AND 33

a 0.44-per-cent solution of sodium chloride was frozen under conditions previously determined to result in efficient agitation.* The ice resulting from this procedure was completely opaque throughout, as indicated in Fig. 31. An extremely interesting phenomenon was observed when this ice cake was closely examined which serves to substantiate further the assumption that the environment from which solid formation occurs materially affects crystal habit.

The crystals at the extreme sides of the block were for the most part uniformly small, and exhibited no clear cut orientation as compared with the transparent product. When ice formation reached a definite point, however, a radical change in the type of crystallization occurred sharply. The ice no longer formed as distinct crystals at the solid crystal face, but as small round pellets, which completely filled the central part of the cake. The sharpness of this formation and some idea of its general nature are shown in Figs. 32 and 33. The manner in which the ice cake was cut to obtain the photographs is indicated in Fig. 34. In Fig. 35 is shown the sudden transition between the comparatively solid opaque ice and that forming from the more concentrated salt solution. The individual nature of these aggregates is clearly indicated in Fig. 36.

5. *Summary.*—The formation of opaque ice results whenever conditions affecting the formation of a solid phase are such that optical heterogeneity results. Such a condition may well be occasioned by the formation of a solid phase consisting of an eutectic mixture of ice and salt. When the salt concentration in such a mixture is low, however, no opacity results. In those cases where the salt concentration in the eutectic is high it has been shown that the salt dissolved in the mother liquor from which ice separates reaches a concentration sufficient to occasion opacity due to environmental influences long be-

*The solution was frozen in the experimental ice can described in Chapter II, Section 7; 1.3 cu. ft. of free air was applied during the entire run.

FIG. 35. TRANSITION BETWEEN OPAQUE ICE AND "PELLET" FORMATION IN FREEZING OF 0.4-PER-CENT SODIUM CHLORIDE SOLUTION

fore the eutectic point is reached. In the solutions commonly available for ice manufacture the application of proper chemical treatment so changes the nature of the dissolved salts that eutectic formation will only occur long after the critical concentration occasioning opacity from environmental influence has been reached. Therefore, the environmental effect of the dissolved salts is undoubtedly the primary factor in producing opacity.

To account for this phenomenon an hypothesis has been developed which assumes that as ice forms from a dilute aqueous salt solution continued crystal growth results from the adsorption of additional

FIG. 36. NATURE OF ICE CRYSTALS FORMED FROM A CONCENTRATED SODIUM CHLORIDE SOLUTION

particles from the solution. Such adsorption always includes a definite though small amount of the solute constituents, which increases as the concentration of salt in the solution increases. This continues until the amount of solute adsorption becomes sufficient to effect a

condition of optical heterogeneity in the solid phase by altering the size and orientation of the ice crystals subsequently formed. It follows that for each solution there exists a definite concentration of dissolved salt subsequent separation of ice from which appears opaque. Localized concentration of dissolved salt, due to ineffective agitation of the solution being cooled, therefore, invariably results in the formation of an opaque shell encasing the ice cake. Concentration of the salts dissolved in the unfrozen solution to the critical point invariably results in an opaque core.

On the basis of this hypothesis it seems to be indicated that the prevention of opaque ice formation should be attempted according to three general methods:

(A) The solutions being frozen should be effectively agitated to prevent localized concentration of dissolved constituents, and core water should be removed whenever the homogeneous core solution reaches the critical concentration. A method of this type has been proposed in Chapter II.

(B) The concentration of the dissolved salts should be reduced prior to the freezing operation. This may be accomplished in the case of sodium bicarbonate waters by means of the method described in Chapter III.

(C) New methods of water treatment should be developed whereby the effect of the dissolved salt constituents upon the crystal habit of the ice being formed at the solid interface could be effectively counteracted. No successful methods of this type have so far been developed. It seems possible, however, that further study of the forces operative at the interface between a crystal surface and the aqueous solution with which it is in equilibrium, with the production of transparent ice as a primary object, will yield data upon which successful methods of this type may eventually be developed.

Appendix B

Theoretical Power Loss Incurred in Removal of Core Water

1. *Discussion.*—In the course of the present investigation a method has been developed for actual plant operation wherein it is proposed to remove and completely reject approximately 20 per cent of the water originally subjected to cooling. Such practice has in the past been generally viewed with considerable disfavor by practical operators, who have held that large core removal incurs too great a power loss. It seems advisable, therefore, to determine what per cent of the total power required in the production of a ton of ice from water at 70 deg. F. is required in cooling the additional 400 pounds of water used when a 20-per-cent core is removed. It is assumed that the core water removed at 32 deg. F. is entirely wasted, no attempt being made to effect any degree of heat exchange.

Assuming a brine temperature of 16 deg. F., the amount of heat given up irreversibly to the brine on immersing in it an ice can filled with water at 70 deg. F. may be calculated as follows:*

ΔH_1 = heat liberated in cooling 1 pound of water from 70 to 32 deg. F. ..... = − 38 B.t.u.

ΔH_2 = heat liberated in freezing 1 pound of water at 32 deg. F. ..... = −144 B.t.u.

ΔH_3 = heat liberated in cooling 1 pound of ice from 32 to 16 deg. F. ..... = − 8 B.t.u.
(Specific heat of ice = 0.5)

$\Delta H' = \Delta H_1 + \Delta H_2 + \Delta H_3$ ..... = −190 B.t.u.

In any actual ice plant installation, however, there are, according to Macintire†, several additional factors which must be considered in order to arrive at the total heat removed from the brine by the ammonia coils per pound of ice placed in daily storage. These are tabulated on the basis of a 100-ton ice plant as follows:

ΔH_4 = 10 per cent of $\Delta H'$ for non-computable losses = −19 B.t.u.

ΔH_5 = Heat leakage through insulation = −1.07 B.t.u.

ΔH_6 = Heat removed by the brine in the dehumidifiers from air to be used for agitation = −3.56 B.t.u.

*The ΔH used throughout the discussion is the heat liberated by the water being cooled. The convention as to sign is that proposed by Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923.

†H. J. Macintire, "Handbook of Mechanical Refrigeration," p. 414, John Wiley and Son, 1928.

ΔH_7 = Heat introduced into the brine by the brine agitators = -6.1 B.t.u.

Therefore,

$$\Delta H'_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 \ldots\ldots\ldots = -219.73 \text{ B.t.u.}$$

An amount of heat = $\Delta H'_{\text{total}}$, or -219.73 B.t.u., is therefore absorbed by the brine, and in turn by the liquid ammonia in the ammonia brine coils, in order that 1 pound of water at 70 deg. F. may be converted into ice at 16 deg. F. Furthermore,

If q' = the heat absorbed by the liquid ammonia in the brine coils at a temperature T'

Then $q' = -\Delta H'_{\text{total}}$

= $+219.73$ B.t.u. per pound of ice produced

= $+439460$ B.t.u. per ton of ice produced, assuming no core removed.

By reversing a heat engine it is possible through the expenditure of work to transport heat from a cold to a hot reservoir. This is essentially the method employed in a refrigerating machine. If W' is the work done in removing the heat, q', from a cold reservoir at a temperature T' to a hot reservoir at a temperature T, then for a perfectly efficient machine

$$W' = q' \frac{T - T'}{T'} *$$

If it is assumed that the liquid ammonia in the brine coils must be held at a temperature of 10.55 deg. F., corresponding to a suction pressure of 24.3 lb. per sq. in. (gage), in order to maintain a brine temperature of 16 deg. F., then

T' = 10.55 deg. F.

= 10.55 + 460 or 470.55 deg. F. absolute.

If it is assumed that the temperature of the available condenser water is 75 deg. F. and that the temperature of the liquid ammonia leaving the condenser is 10 deg. F. above that of the water entering the condensers, or 85 deg. F., corresponding to a condenser pressure of 151.7 lb. per sq. in. (gage), then

T = 85 deg. F.

= 85 deg. + 460 deg. or 545 deg. F. absolute.

Applying these conditions to the case of the perfectly efficient refrigerating machine, the amount of work, W', required to re-

*Lewis and Randall, *loc. cit.*, p. 131.

move 439 460 B.t.u. from 470.55 to 545 deg. F. absolute may be calculated as follows:

$$W' = 439\,460 \times \frac{(545 - 470.55)}{470.55}$$

$$= 69\,500 \text{ B.t.u.}$$

$$= \frac{69\,500}{3412} \text{ or } 20.36 \text{ kw.-hr. per ton of ice produced.}$$

It is of course obvious that the actual amount of work required to transport the heat q' from T' to T in the case of any practical machine will be greater than that calculated for the ideal case, since the relative efficiency of a practical compressor departs radically from 100 per cent.

According to Macintire* the actual brake horsepower of an ammonia compressor (indicated horsepower + 10 per cent) operating with a condensing pressure of 151.7 lb. per sq. in. (gage) and a suction pressure of 24 lb. per sq. in. (gage) is 1.13 horsepower per ton of refrigeration. The ton of refrigeration is, by definition, the cooling rate of 12 000 B.t.u. per hr. Assuming calculations to be made on the basis of a plant producing 100 tons of ice every 24 hours by continuous operation, and that 220 B.t.u. (ΔH_{total}) must be removed from the water being frozen per pound of ice produced, it follows that the amount of heat removed in 24 hours is 44 000 000 B.t.u.,

$$= 1\,833\,000 \text{ B.t.u. per 100 tons of ice per hour}$$

$$= \frac{1\,833\,000}{12\,000} \text{ or } 152.8 \text{ tons of refrigeration.}$$

The work required to produce 100 tons of ice in 24 hours would therefore be

$$1.13 \times 24 \times 152.8 \text{ or } 4143 \text{ hp.-hr.}$$

$$= 41.43 \text{ hp.-hr. per ton}$$

$$= 41.43 \times 0.7457 \text{ or } 30.89 \text{ kw.-hr. per ton.}$$

The actual power required to produce a ton of ice utilizing a practical refrigerating machine operating under the conditions previously assumed would, therefore, be 30.89 kw.-hr. as compared to the 20.36 kw.-hr. required by the previously considered ideal cycle. The indicated efficiency of the actual machine is therefore $\frac{20.36}{30.89} \times 100$ or 65.91 per cent.

Loc. cit., p. 44.

So far it has been assumed that no core water is removed during the freezing process.

The heat liberated on cooling 400 lb. of water from 70 deg. F. to 32 deg. F. is

38×400 or 15 200 B.t.u.

Therefore, the total heat absorbed by the ammonia coils in producing a ton of ice when a 20 per cent core is removed is

439 460 + 15 200 or 454 660 B.t.u.

Therefore, since $q'' = -454\ 660$

$$w'' = -454\ 660 \times \frac{(545 - 470.55)}{470.55}$$

$$= 71\ 930 \text{ B.t.u. per ton}$$

$$= 21.08 \text{ kw.-hr. per ton on the basis of an ideal refrigerating machine}$$

$$= \frac{21.08 \times 100}{65.91} \text{ or } 31.99 \text{ kw.-hr. per ton on the basis of a refrigerating machine operating at 65.9 per cent efficiency.}$$

The added power required when a 20-per-cent core is removed is therefore seen to be

$31.99 - 30.89$ or 1.1 kw.-hr.

The added power represents an increase of 3.56 per cent.

In actual practice the water used to replace the core solution is cooled from 70 deg. F. to 32 deg. F. largely by the melting of ice previously formed. In a 400-lb. ice can the removal of a 10-gallon core leaves a core cavity having the following approximate dimensions: 4 in. $\times$ 15.5 in. $\times$ 55 in. The area of ice thus exposed is 2145 sq. in. To cool the 10 gallons of water from 70 deg. F. to 32 deg. F. requires the melting of 22 pounds of ice representing a layer 0.3 in. thick. This should theoretically increase the total freezing time. Although plant observations have not indicated that any marked increase does occur, the difficulty, if actually present, may readily be overcome by externally precooling the core water to approximately 32 deg. F. before its addition to the core cavity.

In Appendix E it is shown that the average cost of production is \$3.12 per ton, of which the average total power cost is \$0.825. The increase in power of 1.1 kw.-hr. per ton, occasioned by the removal of a 20-per-cent core, is therefore seen to result in an increased total production cost of $1.1 \times \$0.015$ or \$0.016 per ton, an increase on the basis of total cost of $\frac{0.016 \times 100}{3.12}$ or 0.5 per cent.

2. *Summary.*—It has been shown that the removal of core water amounting to 20 per cent of the solution originally subjected to freezing, and its replacement with water at the same temperature as that originally used, results in an increase of power of 1.1 kw.-hr. per ton, which, on the basis of power delivered at $0.015 per kw.-hr., amounts to an increase in production cost of $0.016 per ton or 0.5 per cent of the total production cost.

The increase in total cost thus occasioned is therefore seen to be of such secondary importance that no hesitancy should exist in adopting this measure to prevent the occurrence of opaque ice wherever possible. Furthermore, it is obvious that the increase in power resulting from core water removal will be materially reduced if the cold solution is utilized in suitable heat exchange before being wasted. In a plant producing 100 tons of ice a day, the removal of a 20-per-cent core results in 5000 gallons of water at approximately 32 deg. F. becoming available for this purpose.

Appendix C

Base-exchange Action of Alkaline Earth Zeolites

1. *Introduction.*—The utilization of magnesium zeolite in the treatment of sodium bicarbonate waters, and a summary of the reactions involved, have been previously recorded in Chapter III. A more detailed description of the proposed treatment and available data concerned with its commercial application follows.

2. *History of Zeolite Exchange Reaction.*—As early as 1850 it had been observed that soil possessed the power to remove certain of the dissolved constituents from aqueous solutions which percolated through it. In an endeavor to explain the phenomenon, Way* hypothesized the presence of complex double silicates possessing the ability to exchange a portion of the basic compounds comprising their intricate structure for basic ions existing in solutions with which they came in contact. He was finally able to synthesize silicates possessing this predicted behavior. Eichorn† later established the fact that the course of the exchange was reversible and dependent upon the concentration of the substances involved in the reaction.

Although Way proposed the use of base-exchange material as a fertilizer, the first attempt to utilize the exchange principle occurred in the sugar industry, when it was proposed‡ to replace the sodium and potassium, present in sugar syrups as dissolved salts, by calcium, using calcium zeolite. The corresponding calcium salts were so much less soluble that their precipitation effected a marked reduction in ash content of the resulting molasses. Although the method does not seem to have been developed to any extent, Rumpler§ claims that early experimental results obtained in actual plant demonstrations were extremely promising.

More recent investigations concerning the reversible nature of the reactions involved in zeolite exchange materials have been conducted by Frankforter and Jensen¶ and Jenny.** Both investigations are limited, however, to studies of static equilibrium conditions. The

*Jour. Royal Agric. Soc. vol. 11, p. 313, 1850; vol. 13, p. 123, 1852.
†Pogg. Ann. vol. 15, p. 126. 1858.
‡Harms, German Patent No. 95,447, June 2, 1896.
Rumpler, Deut. Zuckerind. vol. 26, p. 585, 625, 1901.
Z. ver Rubenzucker Ind. pp. 798-809, 1905.
Handbuch der Zuker. frabrikation, p. 298, 1906.
§*Loc. cit.*
¶Chemical Exchange Reactions of a Zeolite, Ind. Eng. Chem. vol. 16, p. 620, 1924.
**Cation and Anion Exchange at Permutit Interfaces, Kolloid chemische Beihefte, vol. 23, p. 377, 1927.

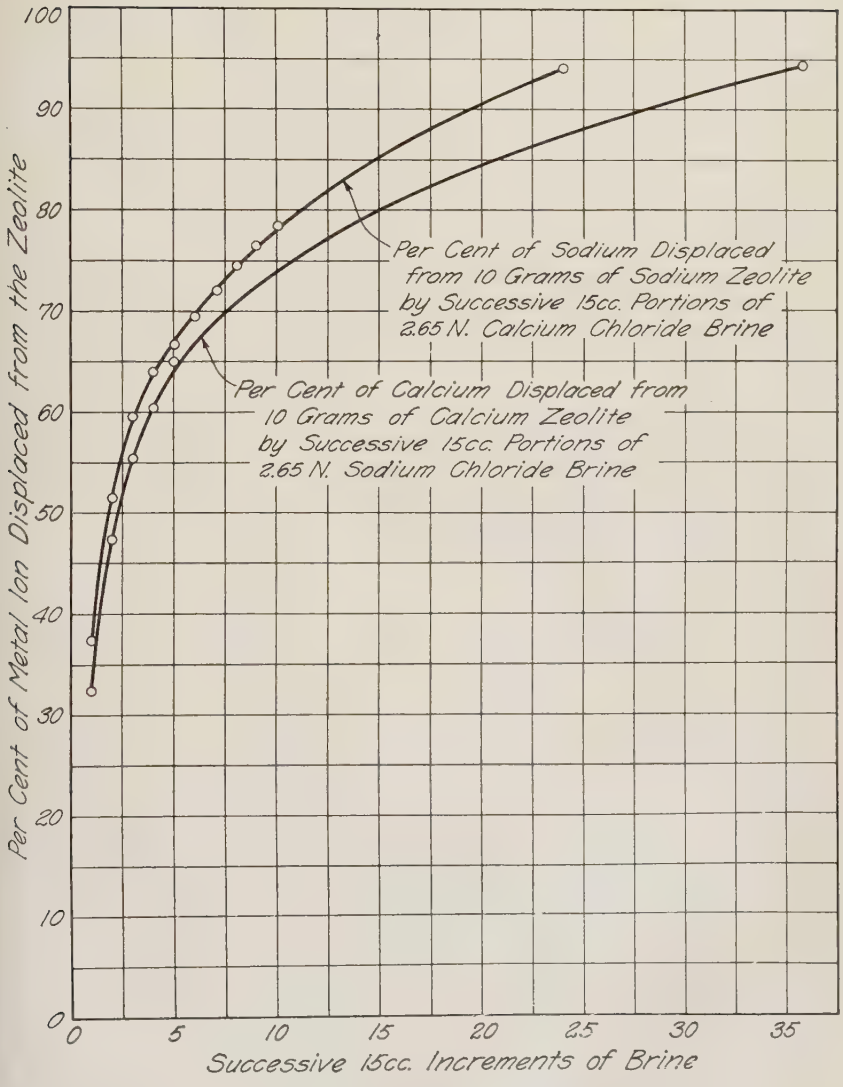

FIG. 37. STATIC EQUILIBRIUM DATA FOR VARIOUS ZEOLITES AND SOLUTIONS—FRANKFORTER AND JENSEN

data of Frankforter and Jensen for calcium chloride solutions in equilibrium with sodium zeolite and for sodium chloride solutions in equilibrium with calcium zeolite are graphically represented in Fig. 37. The more general data of Jenny are plotted in Fig. 38. It should be noted that Jenny's data represent the general case for each system in-

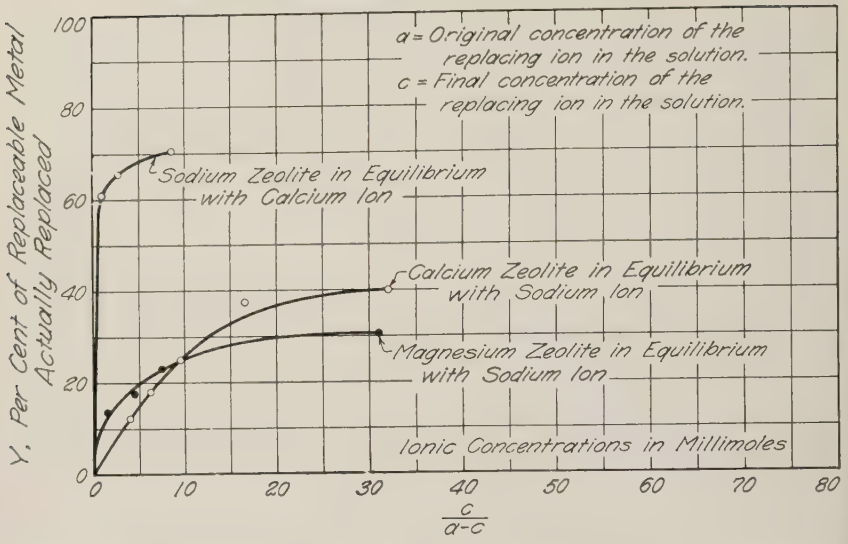

Fig. 38. Static Equilibrium Data for Various Zeolites and Solutions—Jenny

vestigated since the ratio $\frac{C}{A-C}$, plotted against Y in Fig. 38, is independent of concentration.

Previous experience and recorded data, therefore, predict that an alkaline earth zeolite should enter into exchange with sodium ions. The specific points remaining to be determined were (1) whether the concentration and condition of sodium ion existing in naturally occurring sodium bicarbonate water sources is capable of effecting suitable exchange with fully saturated alkaline earth zeolite, (2) whether a sufficient volume of exchange solution is recovered, which, on being treated with lime, yields the reduction of total dissolved salts necessary to produce a suitable grade of ice under standard conditions, thus rendering the method economically feasible, and (3) whether the spent alkaline earth zeolite is completely regenerated by brine solutions prepared from the naturally occurring sodium bicarbonate waters.

3. *Factors Involved in Use of Alkaline Earth Zeolite.*—In the application of alkaline earth zeolites to the present case it has been indicated in Chapter III that the proposed method involves three distinct steps or cycles. After once being used, the alkaline earth zeolite must be regenerated by means of a concentrated alkaline earth brine. After complete restoration of the alkaline earth zeolite the excess brine

held in the interstices of the exchange material must be thoroughly removed by washing with the raw water available. When the unbound alkaline earth salt has been completely removed the effluent solution is accumulated throughout a so-called exchange cycle to be first lime treated and then frozen. Throughout the entire washing cycle some exchange between alkaline earth and alkali metal ions takes place at the zeolite surface, the extent of which increases as the concentration of brine is reduced by the wash water. From the standpoint of exchange the washing and exchange cycles thus overlap. The necessity for complete removal of unbound alkaline earth salt resulting from the brine alone controls the duration of the washing cycle.

Since the amount of exchange at any zeolite surface depends upon the concentration ratio existing between bound alkaline earth and bound alkali metal in the zeolite and between alkaline earth ion and alkali ion in the solution, thus requiring the concentration of alkaline earth salt in the regenerating brine to be high as compared to the other concentrations involved, the cost of the alkaline earth salt used in the preparation of the brine and the subsequent use of the brine itself becomes a controlling factor in the ultimate cost of the process.

Of the four alkaline earth metals only calcium and magnesium in the form of their common salts may be considered as suitable compounds for the production of regenerating brines. Barium compounds are toxic and strontium salts are as yet too expensive. Of the two thus available, calcium has a distinct advantage over magnesium, as calcium chloride is quoted at $20.00 per ton, while the price of the corresponding magnesium chloride is $36.00 per ton (f.o.b. Works).* Thus, although the static equilibrium data of Jenny† indicate that magnesium zeolite is more effective in exchange reactions with sodium ions, the lower cost of calcium chloride led to a preliminary investigation concerning the possible utilization of calcium zeolite.

4. *Preliminary Results.*—The results of this preliminary investigation may be summarized as follows:

In any solution containing bicarbonate ions there exists an equilibrium between carbonate and bicarbonate ions, an equilibrium which is in turn dependent upon the partial pressure of carbon dioxide. The factors controlling the final establishment of equilibrium have been thoroughly investigated by John Johnston and his co-workers.‡ The effect of this specific equilibrium in the use of calcium zeolite with

*Both quotations refer to the April, 1930 Market Report.

†*Loc. cit.*

‡Jour. Am. Chem. Soc. vol. 37, p. 2001, 1915; vol. 36, p. 975, 1916; vol. 49, p. 1235, 1927; vol. 51, p. 2082, 1929.

naturally occurring sodium bicarbonate waters lies in the fact that at the normal concentration of hydroxyl ions existing in such solutions (corresponding in the case of the Crisfield water to a pH of 8.4) calcium carbonate is unstable. This results eventually in the precipitation of calcium carbonate at the surface of the zeolite in sufficient quantities to render the exchange material completely ineffective. It was determined that if the pH of the sodium bicarbonate solution was sufficiently reduced so that calcium carbonate would not precipitate, the predominating exchange was no longer between sodium ions and calcium, but between hydrogen ions and calcium. This condition is to be predicted from Jenny's* data. The use of calcium zeolite was therefore determined to be impracticable in the case of sodium bicarbonate solutions, even though the actual exchange obtained between the calcium zeolite and sodium ions at a pH of 8.4 proved to be extremely acceptable.

With the use of magnesium zeolite, however, no such difficulty exists. In Fig. 39 the equilibrium concentrations of calcium and magnesium ion resulting from calcium carbonate and magnesium hydroxide, the stable solid phase in each case, are plotted against pH.† From these data it is evident that at a pH of 8.4 no precipitation of magnesium hydroxide occurs and that the pH may increase to 9.5 before precipitation will occur in any solution to be encountered in the normal utilization of magnesium zeolite. To establish the various factors involved in the successful utilization of magnesium zeolite with sodium bicarbonate solutions a complete laboratory investigation was undertaken, followed by a semi-plant-scale demonstration at the local ice plant.

5. *Laboratory Investigation of Magnesium Zeolite.*—In the laboratory investigation magnesium zeolite was first prepared by prolonged washing of the commercial sodium compound‡ with a 3-per-cent solution of pure magnesium chloride in distilled water followed by complete removal of brine by continued washing with distilled water. The final magnesium content of the exchange material was 2.5 per cent by weight.§

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*Loc. cit.

†The values for the calcium curve were calculated from the data of Johnston and Williamson (Jour. Am. Chem. Soc., vol. 38, p. 980, 1916). The pH ($= \text{Log } \frac{1}{H}$) values were calculated from hydroxyl ion concentrations in which ionization was considered to be complete; the calcium ion concentrations were calculated on the basis that the degree of ionization was 0.92. The values for the magnesium hydroxide curve were calculated on the basis of the average solubility product ($[Mg]\,[OH]^2 = 8.01 \times 10^{-12}$) calculated from Kline's (Jour. Am. Chem. Soc., vol. 51, p. 2093, 1929) values for the molalites of magnesium and hydroxyl ions.

‡The zeolite material used was of the precipitated gell type.

§The commercial zeolite as obtained was determined to lose 53 per cent of its original weight when dried at 105° C. for 2 hours. The magnesium content is on the dry basis.

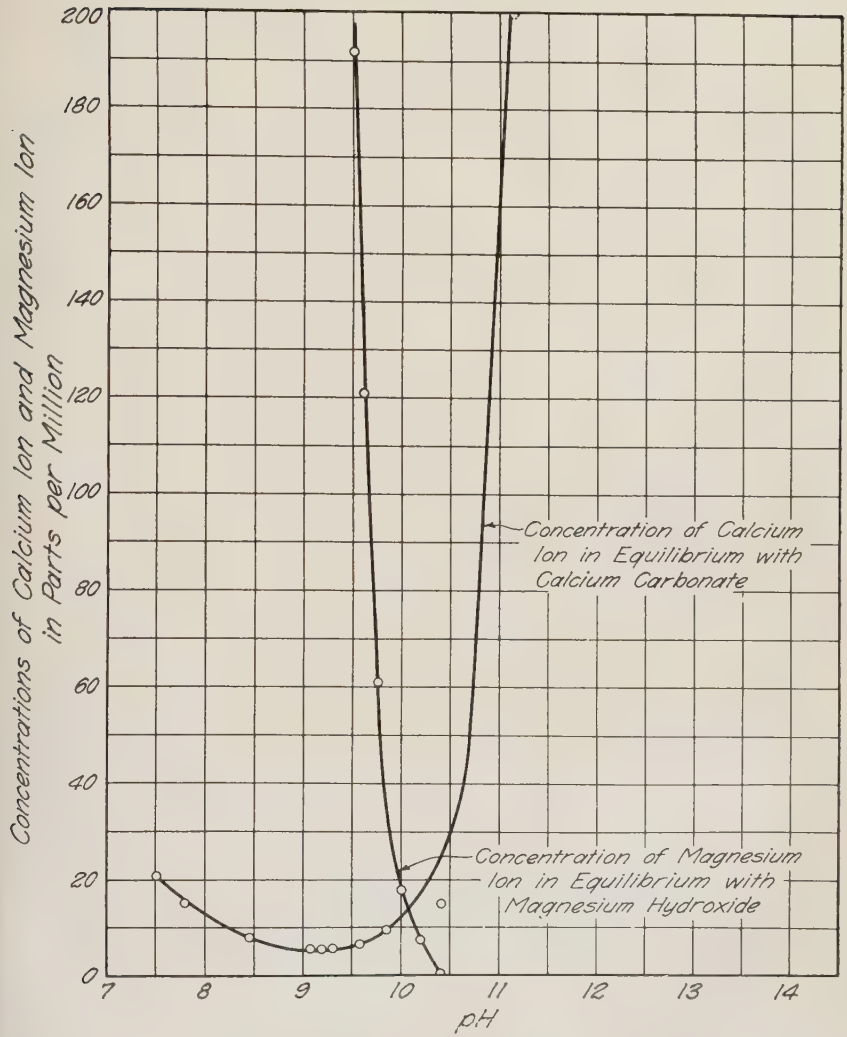

FIG. 39. EQUILIBRIUM CONCENTRATION OF CALCIUM AND MAGNESIUM IONS PLOTTED AGAINST pH

The sodium bicarbonate solution used in all laboratory runs, an analysis of which is shown in Table 10, was synthetically prepared to correspond in composition to the Crisfield water. The zeolite charge was contained in a glass tube 2.8 cm. in diameter and formed an exchange column 34 cm. high. A single charge of zeolite was used throughout the investigation.

TABLE 10

COMPOSITION OF SYNTHETIC CRISFIELD WATER USED IN LABORATORY EXPERIMENTS ON MAGNESIUM ZEOLITE

Ionic Constituents		Concentration, parts per million
Sodium	Na	294
Calcium	Ca	6
Carbonate	CO_3	27
Bicarbonate	HCO_3	580
Sulphate	SO_4	52
Chloride	Cl	57

pH = 8

The magnesium chloride brine used in all subsequent regenerations was prepared by dissolving commercial magnesium chloride* in synthetic sodium bicarbonate solution. The brine concentration was 3 per cent.

The magnesium zeolite, dried in the laboratory atmosphere until its moisture content was approximately 53 per cent and then placed in the exchange tube, was washed with the exchange solution by upward percolation at a rate of 20 cc. per minute. The effluent solution was collected in a series of samples later analyzed for magnesium. The data thus accumulated are shown in Fig. 40. The exchange curve shown in Fig. 1, Chapter III, was prepared on the basis of the data thus obtained.

In Chapter III it was demonstrated that, to use an air supply of 0.12 cu. ft. of free air per min. for agitation, the concentration of magnesium in the effluent exchange solution may not become less than 67 parts per million. If, however, a larger volume of air is used during a 2-hour auxiliary period and at the end of this time the volume of air is reduced to 0.3 cu. ft. per min., a suitable grade of ice can be produced from effluent exchange solutions having a magnesium ion concentration of only 33 parts per million. Since the economic operation of the method has been shown to depend upon the volume of exchange solution which may be collected between consecutive regenerations, subsequent laboratory investigation was concerned with determining the conditions under which such effluent exchange solutions could be effectively produced.

*The magnesium chloride used in both the laboratory and semi-plant-scale experiments was the commercial grade known as magnesium chloride flake supplied to the trade by the Dow Chemical Company of Midland, Michigan. Material, having the following composition, has been quoted at $36.00 per ton, f.o.b. Midland.

Analysis

$MgCl_2 \cdot 6H_2O$	102.71 per cent
$CaCl_2$	0.22 per cent
NaCl	1.34 per cent
SO_4	0.14 per cent

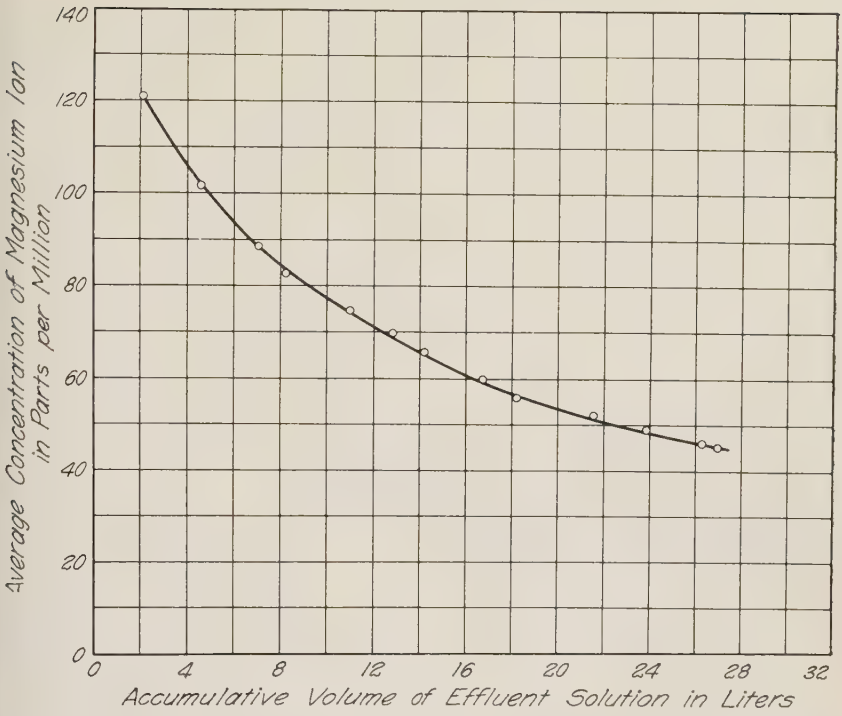

FIG. 40. EXCHANGE CYCLE DATA FOR MAGNESIUM ZEOLITE AND SODIUM BICARBONATE SOLUTION

Following the preliminary exchange, cycle regeneration was effected by washing the zeolite with the 3-per-cent regenerating brine at a rate of 20 cc. per minute. The effluent brine, recovered in a series of successive samples, was analyzed for sodium,* the course of the regeneration cycle being shown graphically in Fig. 41. In Fig. 41 the initial increase of sodium results from dilution by the exchange solution remaining from the previous run. The more general form of the curve results from the fact that as the concentration of magnesium increases in the zeolite subsequent regeneration afforded by the fixed ratio of $\frac{\text{magnesium}}{\text{sodium}}$ in the brine decreases. It is evident that the major portion of the regeneration is thus afforded by the first portions of brine used. It is also obvious that the latter portion of effluent brine, although possessing a higher ratio of $\frac{\text{sodium}}{\text{magnesium}}$ than the original

*The sodium concentration was determined by the uranyl-zinc acetate method proposed by Barber and Kolthoff, Jour. Am. Chem. Soc. vol. 50, p. 1625, 1928.

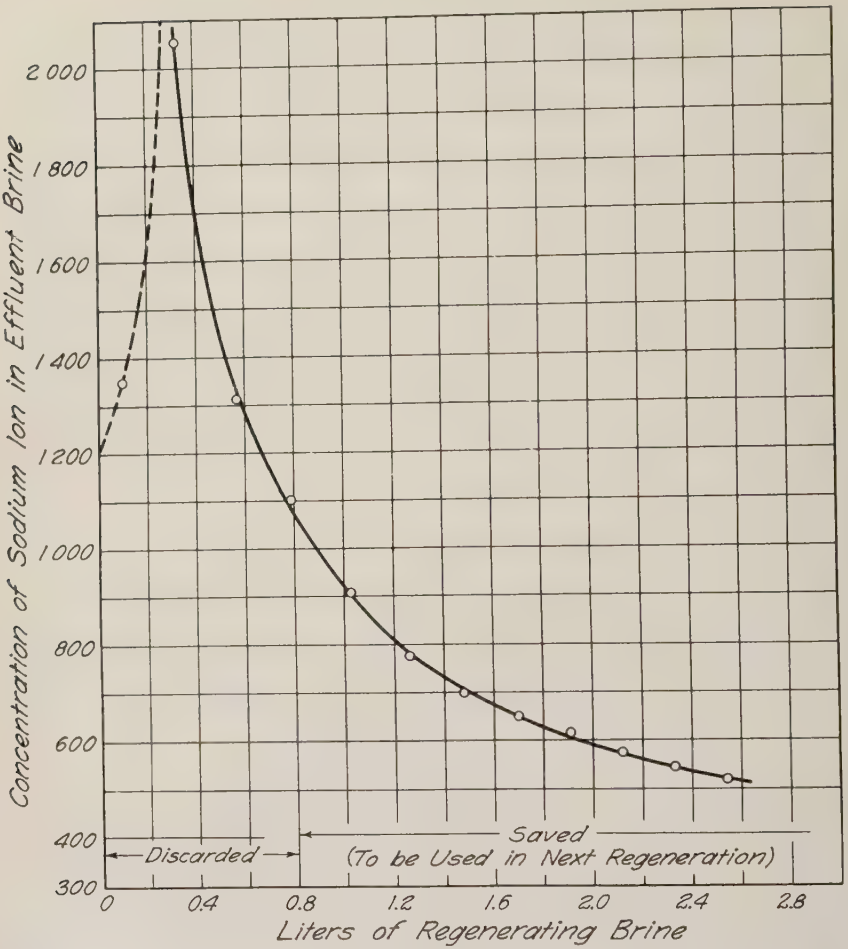

Fig. 41. Regeneration Cycle Data for Magnesium Zeolite

3-per-cent solution, still possesses regenerative properties under conditions wherein the ratio of $\frac{\text{magnesium}}{\text{sodium}}$ in the zeolite is low. The most effective use of regenerative brine would therefore be one in which only the first portion of effluent regenerative solution is discarded, the latter being used as the first solution to be passed through the depleted zeolite column in the following regeneration cycle. After using the recovered brine in the next regeneration a volume of fresh brine equivalent to that previously discarded would complete the cycle. Thus the total volume of brine used during each cycle remains con-

stant, the actual brine requirements for regeneration being merely that volume of brine discarded.

Consequently, in the run, the regenerating-cycle data of which are shown in Fig. 41, the first 800 cc. of brine were discarded as indicated. When an additional 1860 cc. had been used the concentration of sodium in the effluent solution was determined to be approximately equivalent to that in the fresh brine. Although subsequent analysis indicated that at this point some sodium was still being displaced from the zeolite, later investigation established the fact that this approximation adequately answers the demands of practical operation. The 1860 cc. of brine thus recovered was saved to be used in the next regeneration cycle.

Washing of the zeolite column was effected by means of the synthetic exchange solution. The course of the washing cycle was followed by determining the concentration of chloride ion in successive 100 cc. portions of the wash water, any concentration in excess of that present in the original wash water being considered equivalent to the concentration of unbound magnesium chloride present. The course of the washing cycle is shown in Fig. 42. The concentration of chloride ion in the original wash water being 55 parts per million, it is evident that the washing was complete when 1400 cc. of solution had passed through the column. The washing rate of 50–60 cc. per minute used was high as compared to that used during regeneration. The purpose of the high rate was twofold: (1) to decrease the amount of exchange, and (2) to prevent channeling.

The exchange solution was then run through the column at a rate of 20 cc. per min. until the average concentration of magnesium in the effluent water was 33 parts per million. The volume of exchange solution thus recovered was 27.026 liters. While this volume of recovered solution is less than would be predicted from Fig. 40, it more nearly approximates actual operating conditions. In the former case the magnesium zeolite was prepared by prolonged washing with a solution of pure salt in distilled water in which no appreciable concentration of sodium existed. Under actual operating conditions the concentration of sodium in the regenerative brine, resulting from both the sodium bicarbonate water and the commercial magnesium chloride, is comparatively high. The final magnesium content of the regenerated zeolite (2.3 per cent) is therefore not as high as that of the material used in the exchange cycle previously described. This is substantiated by the fact that in subsequent runs an identical volume of exchange solution (27 liters) was recovered having an average magnesium ion

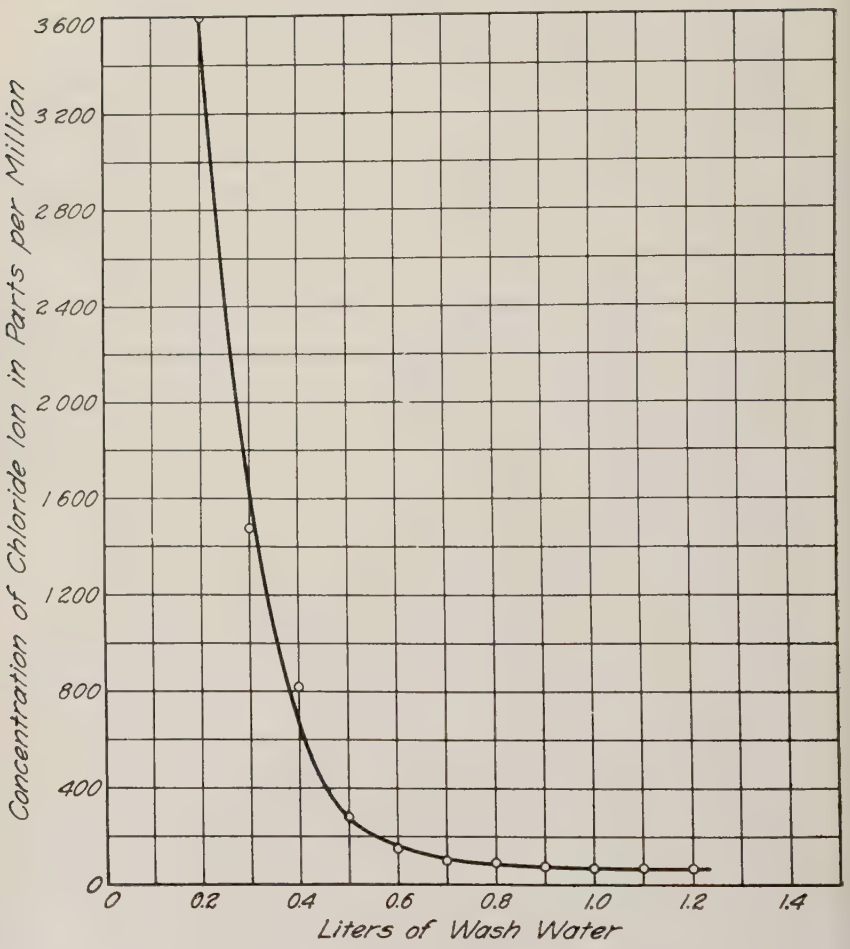

Fig. 42. Washing Cycle Data for Magnesium Zeolite

concentration of 33 parts per million. In the run immediately following, for example, the zeolite was regenerated by first passing through the column the 1860 cc. of brine recovered from Run 2, and then following with 800 cc. of fresh brine. Washing was again complete when 1400 cc. of wash water had been used. The volume of effluent exchange solution having an average magnesium ion concentration of 33 parts per million was 27 liters.

The complete effectiveness of discarding only the first portion of regenerating brine was finally demonstrated when the zeolite column was regenerated by means of 2660 cc. of fresh 3-per-cent brine. After

a washing cycle comprising 1400 cc. of wash water the volume of exchange solution having an average magnesium ion concentration of 33 parts per million was again 27 liters. In any complete cycle, therefore, the cost of the process is entirely dependent upon the ratio existing between the volume of brine that must be discarded to the volume of exchange solution recovered. On the basis of the data accumulated, wherein 800 cc. of 3-per-cent brine produces 27 liters of an exchange solution, 7.85 pounds of commercial magnesium chloride would produce 1000 gallons of treated water.

6. *Summary of Laboratory Investigation.*—In summarizing the laboratory results obtained the following points are thus seen to have been established:

(1) Effective exchange is obtained under the conditions to be expected in practical operation.

(2) Efficient regeneration can be effected by a procedure wherein only the first portion of the regenerating brine is discarded, the additional brine used being utilized in the regeneration cycle following.

(3) Controlled operation should be accomplished by metering the volume of solutions employed in the various phases of the process, since in successive runs each of the three distinct cycles continues to either require or produce the same volumes of solution.

7. *Semi-plant-scale Operation.*—To check the laboratory results semi-plant-scale runs were conducted at the local ice plant wherein actual Crisfield water was used instead of synthetic solutions. Three 150-gallon tanks limited unit capacity, the water to be treated being transferred from one tank through a suitable zeolite column into a second where liming was effected. Following liming and settling the solution was then pumped through a plate filter into a third tank, where neutralization by aluminum sulphate completed the treatment. Following a second filtering the treated water was transferred to ice cans and frozen under actual plant operating conditions.

The first plant runs were undertaken to check the evidence presented in Chapter III which was obtained when synthetic water samples were frozen which corresponded in chemical composition to solutions resulting from the liming of exchange effluents having an average concentration of magnesium ion of 106 parts per million. Such solutions represent the maximum decrease in total solids possible when the magnesium zeolite method is utilized in the case of the Crisfield water.

The zeolite material used had a volume of 907 cu. in., weighed 22 lb. (as received), and formed an exchange column 4 in. in diameter and 72 in. high. The production of the magnesium zeolite from the commercial sodium compound was effected by passing 65 gallons of 3 per cent magnesium chloride brine* through the column. The concentration of magnesium in the resulting zeolite was 2.3 per cent. This material after being washed produced 102.5 gallons of solution having an average magnesium ion concentration of 105 parts per million. Regeneration required 25 gallons of fresh 3-per-cent brine and yielded a column which produced 100 gallons of solution having an average magnesium ion concentration of 109 parts per million. These solutions on being efficiently lime treated and neutralized produced, in standard cans using 0.1 cu. ft. of free air per min., ice which was entirely comparable to that resulting from the synthetic samples having the same composition.†

On the basis of the 25 gallons of fresh 3-per-cent brine previously cited as being required in the regeneration cycle, and assuming that the same ratio of brine to be discarded to brine to be used in the next cycle $\left(\frac{800}{1860}\right)$ obtained in laboratory experiments holds equally well under plant conditions, it follows that the amount of commercial magnesium chloride required to treat 1000 gallons of Crisfield water is 40.5 pounds.

The exchange rate (530 cc. per min.) used during these first plant runs was, however, slower than that used in the laboratory experiments. Assuming the rate to be directly proportional to the weight of zeolite used in both cases, the plant rate should have been 1438 cc. per min. Furthermore, the manufacturers of the zeolitic material used recommend in the case of the exchange reaction between sodium zeolite and calcium or magnesium ions that the rate should be such that a volume of water equal to the volume of zeolite used should pass through the column in 4.5 minutes. On this basis the plant rate should have been 2930 cc. per minute. The matter of rate during the exchange cycle is of importance since it is to be anticipated that the degree of exchange decreases as the rate at which the exchange solution passes the zeolite surface increases.

The final semi-plant-scale operations were, therefore, designed to study the conditions under which solutions possessing an average magnesium ion concentration of 33 parts per million could be effectively produced at standard exchange rates.

*Prepared by using actual Crisfield water and Dow magnesium chloride.
†See Fig. 19, Chapter III.

In order to accommodate the exchange solution in the storage tanks available, a smaller column of zeolite, containing 5.14 pounds of commercial sodium zeolite, and having a volume of 248 cubic inches, was used in a metal column 4 in. in diameter and 20 in. high. Forty gallons of 3-per-cent brine, produced from raw Crisfield water, was used to form the magnesium compound. The rate at which the brine was passed through the zeolite column was 400 cc. per min. The first 21 gallons of the effluent brine was discarded, the last 19 gallons being saved to be used in the next regeneration cycle. The column was then washed with raw Crisfield water until the unbound magnesium chloride had been completely removed, the volume required being 12 gallons. The rate during the washing cycle was raised to 2800 cc. per min.

In the exchange cycle the rate was maintained at between 800 and 1000 cc. per min., thus becoming equivalent to that recommended in the case of commercial sodium zeolite performance. The exchange cycle was stopped when the average concentration of magnesium in the effluent solution was 33 parts per million. This point was determined nephelometrically according to the method proposed by Feigl and Paevelka* and developed by Kriss.† The volume of exchange solution recovered was 94 gallons.

If, on the basis of zeolite material used, direct proportionality had existed between laboratory and plant runs, the volume of exchange solution produced would have been 136 gallons. The exchange rate was, however, 2.3 times greater than that used in the laboratory. The higher rate was used in all subsequent plant runs in order that the performance of magnesium zeolite could be readily correlated with the engineering data previously accumulated in the case of commercial sodium zeolite installations.

The recovered solution was treated with lime, 2 grains per gallon of ammonium alum being used to produce a suitable floc. The amount of lime used was 20 per cent in excess of theoretical requirements. After agitation followed by a 4-hr. settling period the solution was determined to have the composition shown in Table 11. The solution was then filtered and neutralized by means of aluminum sulphate. This required 3.4 lb. of aluminum sulphate per 1000 gallons of water treated. The solution after neutralization and filtering contained 660

*Microchemie, vol. 2, p. 88, 1924.

†Biochem. Zeit. vol. 162, p. 359.

Note: The method consists in precipitating magnesium as magnesium ferrocyanide by adding ammonium ferrocyanide to a solution containing magnesium ions which has previously been diluted with an equal volume of 95 per cent ethyl alcohol. The concentration of the stable, micro-crystalline precipitate thus formed is then determined according to standard nephelometric procedure.

TABLE 11

COMPOSITION OF TREATED WATER RESULTING FROM APPLICATION OF LIME AND ALUM TO EFFLUENT EXCHANGE SOLUTION HAVING AVERAGE MAGNESIUM CONCENTRATION OF 33 PARTS PER MILLION

Ionic Constituents		Concentration, parts per million
Calcium	Ca	4.0*
Magnesium	Mg	1.4*
Sodium	Na	220.0
Carbonate	CO_3	144.0
Hydroxide	OH	34.0
Chloride	Cl	57
Sulphate	SO_4	52
Silica	SiO_2	12
Total		519.0

*To compare the effectiveness of this treatment with that to be expected in practice see Appendix D.

parts per million of total solids, representing a decrease of 289 parts per million or 30 per cent.

The water finally recovered was frozen under the following plant operating conditions:

(1) Standard can.
(2) Standard high pressure drop tube shown in Fig. 4a, Chapter II.
(3) Auxiliary air, applied to the standard drop tube, amounting to 1.3 cu. ft. of free air per min. for the first 2 hours. Auxiliary air supplied before the can was placed in the brine.
(4) Regular air, applied to same drop tube designated in (3), amounting to 0.3 cu. ft. of free air per min. for the remaining 44 hours.
(5) Initial brine temperature, 14 deg. F.
(6) Average brine temperature, 15.5 deg. F.
(7) Cores removed:
    (a) 10 gallons after 16 hours of total elapsed freezing time;
    (b) 0.5 gallon after 40 hours of total elapsed freezing time.

The appearance of the product is shown in Fig. 22, Chapter III.

In order to regenerate the column the final 19 gallons of core water recovered from the previous regeneration cycle were passed through the zeolite column, followed by 4 gallons of fresh brine. Since only the first 4 gallons of the effluent brine were discarded the cost of the

TABLE 12

COST DISTRIBUTION OF WATER TREATMENT FOR MAGNESIUM ZEOLITE METHOD

Treatment	Cost
1. Zeolite treatment, (20.3 lb. of commercial magnesium chloride at $0.018)	$0.365 per 1000 gallons
2. Lime and alum treatment (on the basis of $0.015 per ton on 250 gallons)	0.060 per 1000 gallons
3. Neutralization with aluminum sulphate (3.4 lb. at $0.019)	0.065 per 1000 gallons
Total	$0.490 per 1000 gallons

complete cycle is based upon this consumption of regenerating material.

The column was then washed with the raw Crisfield water. In order to effect a further saving in regenerating brine the first 4 gallons of wash water, being high in magnesium chloride,* were saved to be used in preparing fresh brine. The volume of wash water required to effect complete removal of unbound brine was 8 gallons.

It should be noted that in the former run the volume of wash water required was 12 gallons. This discrepancy is accounted for on the basis of the fact that in the former run the zeolite column was not drained, while in the latter case the brine was completely drained from the column before the wash water was applied.

In the exchange cycle which followed the rate was again maintained at between 800 and 1000 cc. per min. The volume of exchange solution having an average magnesium ion concentration of 33 parts per million was 96.5 gallons. Following lime treatment the solution recovered was comparable in composition to that shown in Table 11.

8. *Cost Data—Semi-plant-scale Runs.*—The cost of effecting a reduction of total dissolved solids amounting to 280 parts per million, or 30 per cent, is seen to depend upon the use of 4 gallons of 3-per-cent brine in the production of approximately 95 gallons of treated water. In addition, there results the cost of lime treatment and alum neutralization. The distribution of the total cost of water treatment is given in Table 12.

9. *Time Distribution in Cycles.*—The distribution of time required for the various cycles in the final semi-plant-scale operation is given in Table 13. By varying the volume of zeolitic material used the total time cycle may be readily adjusted to conform to requirements best suited for specific plant operating conditions.

*Refer to Fig. 42.

TABLE 13

TIME DISTRIBUTION BETWEEN VARIOUS CYCLES REQUIRED IN MAGNESIUM ZEOLITE METHOD

Cycle	Time
1 Regeneration cycle 23 gal. at 388 cc. per min.	3.75 hr.
2 Washing cycle 8 gal. at 2.5 liters per min.	12 min.
3 Exchange cycle 95 gal. at 900 cc. (average) per min.	6.65 hr.
4 Time required for complete cycle	10.6 hr.

Note: The time data given were obtained on the basis of a zeolite column having a volume of 248 cu. in. and weighing 5.14 lb. (as received). To maintain the same time cycle and produce 1000 gallons of treated water, a column having a volume of 1.51 cu. ft. and weighing 54 lb. would be required.

10. *Summary of Semi-plant-scale Runs.*—In summarizing the final semi-plant-scale operations the following conclusions may be stated:

(1) The efficient use of commercial exchange material yields results which are effective in rendering characteristic sodium bicarbonate waters available for raw water ice manufacture when standard freezing equipment is employed.

(2) An exchange rate comparable to that utilized in commercial sodium zeolite installations may be used with magnesium zeolite.

(3) Effective regeneration is afforded when commercial magnesium chloride, dissolved in the raw water available, is used to prepare the regenerating brine, and when only the first portions of the effluent brine are discarded.

(4) Metering should afford an accurate control of operation during the various cycles employed.

(5) The method promises to be economically practical.

Appendix D

General Efficiency of Lime Treatment

Since the effectiveness of the proposed magnesium zeolite method depends upon the reduction of dissolved salts in the solutions being treated the lime softening subsequently employed should operate at its highest efficiency. In the past lime treatment has been confined largely to the preparation of boiler make-up water and domestic supplies, wherein a comparatively high residual concentration of calcium carbonate and magnesium hydroxide was not objectionable. Available literature* indicates that at least until recently the lowest residual concentration of magnesium and calcium resulting from cold continuous lime treatment is from 30 to 40 parts per million (calculated as calcium carbonate), and that in common practice from 50 to 60 parts per million more frequently results.

In the course of semi-plant-scale operations conducted in developing the magnesium zeolite method, however, residual concentrations of calcium carbonate equal to 10 parts per million and of magnesium hydroxide equal to 3 parts per million, representing a final concentration of total hardness of 13 parts per million, were consistently obtained when the effluent exchange solutions were batch limed.† A survey was therefore made of efficiently operated lime treatment installations in various sections of the country in order to determine whether such performance could be expected in continued plant-scale operation. The data collected are shown in Table 14. As far as could be determined these data resulted from normal operation. It is of course obvious that strict attention had been paid to efficient control. Since these data were collected the water treatment at the local ice plant, The Twin City Ice and Cold Storage Company, has been carefully followed and has been determined to consistently produce treated solutions in which the combined calcium carbonate and magnesium hydroxide does not exceed 16 parts per million.

Since it has been demonstrated that by far the greatest factor in the production of opaque ice is the total concentration of salts dissolved in the solution to be frozen, it is extremely desirable that the

*Sheppard T. Powell, Jour. Am. Water Wks. Assoc. Vol. 10, No. 1, p. 8. Jan. 1923.
Charles P. Hoover, Am. Soc. Civil Engineers Proceedings, Feb. 1928.
Behrman and DeCelle, Water Softening, National Lime Assoc., 1925, p. 84.
Hoover, Hansley and Shelly, Ind. and Eng. Chem. vol 20, p. 1102, 1928.
A. M. Buswell, The Chemistry of Water and Sewage Treatment, p. 114. The Chem. Catalogue, New York, 1928.

†See Table 11, Appendix C.

Table 14

Residual Hardness of Treated Water in Efficiently Operated Lime Softening Installations

Sample Number	Treatment	Type	Ca p.p.m.	Mg p.p.m.	Combined $CaCO_3$ $Mg(OH)_2$	Remarks
1	Lime and sodium aluminate	Continuous International sand filter	1.6	2.2	9.3	Approximately 4-6 hour settling period.
2	Lime and soda ash	Neckar Water Softener Corp. System	2.2	2.4	10.8	Hot process treatment. Boiler water recirculated to water softener. Reaction temperature 205 deg. F.; retention time 1.6 hrs.
3	Lime, soda ash, sodium aluminate	International Continuous Softener	6.3	0	16.0	
4			4.3	1.4	14.4	
5	Lime, soda ash, sodium aluminate, iron sulphate	Scaife Intermittent Cold Process Softener	5.6	1.55	18.0	40 000 gallon treated in one batch. 1.5 hours agitation period. 1.5 hours settling period. Temp. of treatment 35° F. Settling time 4-6 hours. Raw water from Ill.-Mich. Canal. Canal froze over day after sample taken.
6	Lime, soda, sodium aluminate	Continuous Dodge Softener	4.45	1.25	13.0	
7	Lime, soda ash, sodium aluminate	Scaife Intermittent Cold Process Softener	3.2	0.55	9.3	

Sample 1—Twin City Ice and Cold Storage Company, Champaign, Illinois. Analysis made at University of Illinois. Samples for analysis: 1 liter in duplicate.
Sample 2—Central Illinois Power Company, Peoria, Illinois. Analysis made at University of Illinois. Sample for analysis: 1 liter in duplicate.
Sample 3—Wheeling Still Company, Portsmouth, Ohio. Analysis submitted by National Aluminate Corporation, Chicago.
Sample 4—Old Dominion Company, Globe, Arizona. Analysis submitted by National Aluminate Corporation, Chicago.
Sample 5—Rockford Electric Company, Illinois. Sample submitted by the National Aluminate Corporation, Chicago. Analysis made at the University of Illinois. Samples for analysis: 1 liter in duplicate.
Sample 6—Ottawa Silica Company, Ottawa, Illinois. Sample submitted by the National Aluminate Corporation, Chicago. Analysis made at University of Illinois. Samples for analysis: 1 liter in duplicate.
Sample 7—Hope Natural Gas Company, Cabein Creek Junction, West Virginia. Sample submitted by the National Aluminate Corporation, Chicago. Analysis made at University of Illinois. Samples for analysis: 1 liter in duplicate.
Note: In the case of samples analyzed at the University of Illinois the procedure followed was to evaporate 1 liter of the solution to dryness and to determine calcium and magnesium gravimetrically.

conditions resulting in continued production of lime-treated water containing a minimum concentration of residual "hardness" should be determined. Unfortunately, sufficient data are not available to make it possible to define accurately these optimum conditions. From Fig. 39, Appendix C, it is evident that the minimum solubility of calcium carbonate, 14.5 parts per million, results at a pH of 9.2, while the solubility of magnesium hydroxide may be decreased below 1 part per million when the pH is raised above 10.4. These data are, however, based upon the solubilities of the individual salts. To establish the conditions under which a minimum concentration of the mixed salts would result following lime softening requires additional data especially since the system, in the case of any natural water supply, is further complicated by the presence of varying amounts of such extraneous salts as sodium chloride, sulphate, and carbonate. Future work in the present investigation will be concerned with obtaining the data required in order to define the conditions necessary to invariably produce efficient operation.

Appendix E

Comparative Cost Distribution

1. *Introduction.*—Numerous modifications in operating procedure have been proposed, the practical value of which depends upon the increase in production cost occasioned by their utilization. An attempt therefore has been made to summarize cost distribution in ice plants wherein average standard production methods are employed, and to compare with it the estimated cost distribution in the case of the two methods described in Chapters II and III. As such data have not been readily available the average cost distribution presented is based largely upon information gathered from random sources and assumed generalizations. It is believed, however, to closely approximate that resulting under average operating conditions and as such to serve the purpose intended.

2. *Cost Data for Proposed Methods.*—The method described in Chapter II is characterized by:

(1) The use of a new type of ice can.
(2) The neutralization of the water by means of aluminum sulphate (or sulphuric acid).
(3) The use of a large volume of air during an auxiliary air period.
(4) The removal of a large core.

Although the can which seems to more nearly approximate the ideal case has not as yet been subjected to rigid inspection from the standpoint of large-scale production, the estimated cost of the 300-lb. can actually constructed has been quoted at $8.00 per can in lots of 500 or more. This represents an increase of approximately $0.50 per can over the standard article now supplied to the trade. Assuming a life of five years, during which period each can should produce a total of 90 tons of ice (assuming a 240-day season per year), the increase in production cost occasioned by the use of the new can is $0.005 per ton.

Neutralization of the 300 gallons of Crisfield water necessary in the production of a ton of ice when a 20-per-cent core is removed requires 1.3 pounds of aluminum sulphate, or 1.68 pounds of 66 deg. sulphuric acid. With aluminum sulphate at $0.019 and 66 deg. acid at $0.016 per pound the cost of neutralization is $0.025 per ton in the former case, and $0.027 per ton in the latter. While the use of sulphuric acid is theoretically the more desirable it is assumed that aluminum sul-

phate is used due to the fact that use of acid might arouse adverse public opinion.

The increase in production cost occasioned by the use of auxiliary air may be determined as follows: Standard high pressure air requirements, wherein the air is compressed to 30 pounds (gage) at the compressor and delivered to the air laterals at 20 pounds (gage) are approximately 0.3 cu. ft. of free air per min. per can. A plant having a capacity of 100 tons of ice per day operating at a brine temperature of 16 deg. F. requires 980, 11-in., 400-lb. cans. The freezing period resulting under the conditions noted is approximately 48 hours. The volume of air required for standard operation is therefore 294 cu. ft. per min. This requirement can be delivered by one 16 in. x 10 in. compressor operating at 155 r.p.m. and a power demand of 35 b.h.p., or 26 kw. Therefore, the power requirement per ton of ice is $\frac{26 \times 24}{100}$ or 6.24 kw.-hr. Assuming power to be available at \$0.015 per kw.-hr., the cost of power for air agitation per ton of ice under standard operation is \$0.094. In the special case where 1.3 cu. ft. of air per min. is used for the first two hours of the freezing period, to be followed by 0.3 cu. ft. per min. for the remaining 46 hours, the total air requirements for the plant are 335 cu. ft. per min. This volume of air is supplied by a 17 in. x 10 in. air compressor running at 150 r.p.m. The power demand in this instance is 37 b.h.p. or 27.6 kw., the power required per ton of ice produced being $\frac{27.6 \times 24}{100}$ or 6.62 kw.-hr. The cost of power, again assumed at \$0.015 per kw.-hr., is \$0.0993 per ton of ice produced, representing an increase of \$0.005 per ton over standard requirements.

The removal of the 20-per-cent core required by the proposed method has been shown in Appendix B to amount to an increase in power requirements of 1.1 kw. per ton, representing an increase in production cost of \$0.0168 per ton.

In the case of the proposed mechanical method the added cost of production is therefore seen to amount to \$0.0445 per ton.

The zeolite water treatment method is characterized by:

(1) The use of standard cans.

(2) Treatment of the water, first with magnesium zeolite until the average concentration of magnesium ion in the effluent solution amounts to 33 parts per million, then with lime and alum, and finally with aluminum sulphate (or sulphuric acid).

(3) The use of a large volume of air during an auxiliary air period.

(4) The removal of a large core.

The cost of adequate zeolite treatment followed by lime and alum softening and aluminum sulphate neutralization has been shown in Appendix C to amount to \$0.49 per 1000 gallons of treated water. On the basis of 300 gallons of treated water per ton of ice produced, the cost of water treatment in the second method is \$0.147 per ton.

The extra costs of air agitation and power required for core removal are the same as those previously mentioned in the case of the mechanical method, namely \$0.005 and \$0.016 per ton, respectively.

Therefore, in the case of the proposed magnesium zeolite method the added cost of production is seen to be \$0.163 per ton of ice produced.

3. *Cost Data in Standard Procedure.*—A comprehensive estimate of cost distribution in large-scale standard operation has been compiled by Whyte,* who assumes as his basis a plant having a capacity of 220 tons of ice per day. In this estimate, however, the total cost of electric power is placed at \$0.45 per ton. Since this value is obviously intended to include all auxiliaries, as well as the actual power consumed for refrigeration, it is felt to be too low to represent the average condition existing in the industry. The rate at which power is available is not stated. Since the power rate varies depending upon the nature of its production it has seemed advisable to recalculate the total power cost on the basis of a rate more nearly applying in the case of the average installation. According to H. J. Macintire† a complete power load of between 50 and 60 kw.-hr. per ton of ice produced approximate average requirements. Assuming a complete power load of 55 kw.-hr. and a power rate of \$0.015 per kw.-hr., the average power cost would be \$0.825 per ton of ice produced.

An addition to Whyte's data has been made in the item covering water treatment. It has been assumed that standard lime and alum softening followed by alum neutralization, a procedure practically standard in the ice industry, can be effected under conditions of continuous operation for \$0.015 per ton of ice produced.

4. *Comparative Cost Distribution Data.*—In Table 15 the amended data for standard procedure are tabulated in comparison with the cost distribution for the two proposed methods.

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*H. J. Whyte, Manufacturing Cost in Ice Plants, Bulletin No. 16, National Association of Practical Refrigerating Engineers.

†Associate Professor of Refrigeration, University of Illinois. Private Communication.

TABLE 15

TOTAL COST DISTRIBUTION OF THE TWO PROPOSED METHODS FOR TREATMENT OF SODIUM BICARBONATE WATERS COMPARED WITH THAT INVOLVED UNDER STANDARD OPERATING CONDITIONS

On basis of 200-ton plant

Item of Cost	(1)	(2)	(3)
General expenses, including insurance, taxes, depreciation, and interest on investment (14 per cent)	1.68	1.68	1.68
Plant labor	0.10	0.10	0.10
Tank room labor	0.10	0.10	0.10
Day storage room labor	0.06	0.06	0.06
Power	0.825	0.825	0.825
Excess power for auxiliary air	0.0	0.005	0.005
Excess power for core removal	0.0	0.0165	0.0165
Ammonia	0.050	0.0500	0.0500
Water and other supplies	0.05	0.05	0.05
Maintenance	0.15	0.15	0.15
Salary of portion of crew during 4 months shut-down period	0.088	0.088	0.088
Water treatment	0.015	0.025	0.147
	$3.12	$3.1495	$3.2715

(1) Standard Procedure
(2) Mechanical Method (described in Chapter II)
(3) Magnesium zeolite Method (described in Chapter III and Appendix C)

5. *Economic Value of Proposed Methods.*—In order to indicate the economic possibilities of the proposed methods the conditions existing at an ice plant will be summarized where the only water available is of the sodium bicarbonate type.

This plant is owned by a public service company which in addition distributes light and power in the town in which the plant is located. The local well water has never been successfully utilized in the production of a marketable grade of raw water ice in spite of numerous previous attempts, and the electric power required in both the ice plant and the town is generated locally from steam. All local power requirements could, however, be served much more efficiently by means of electricity generated in a central station and delivered to the town and plant by means of a transmission line. A power transmission line is, in fact, maintained to within sixteen miles of the town at the present time. Use of such power is rendered unavailable solely by the need of distilled water in the production of clear ice. It has been estimated that a saving of approximately $17 500 a year in operating expenses alone would result if the local water could be effectively used in an electrified plant. The use of either of the two methods proposed as the result of the present investigation would allow complete electrification to be established. Since the amount of ice produced annually at the plant is approximately 19 200 tons, a saving of $0.90 per ton would be realized.

Appendix F

General Application of Methods Developed in Course of Investigation

1. *Introduction.*—The statement was made in Chapter II that, although the present investigation has been confined to a study of conditions resulting from the use of sodium bicarbonate waters in electrified ice plants, the mechanical method developed has a much broader application to the ice industry as a whole. The limits to which the concentration of salts dissolved in the solution being frozen at normal brine temperatures may be increased before air agitation efficiently applied is unable to prevent the formation of opaque ice has neither been ascertained nor approximated. It is equally true that when sufficient air agitation is effectively applied no prediction may as yet be made concerning the limits to which brine temperatures may be lowered even in the case of those solutions which, under standard production methods, are now limited to brine temperatures approximating 16 deg. F., due to the fact that lower temperatures occasion opacity. Promising as may be the utilization of water sources which are now completely unavailable it seems extremely probable that any method which will facilitate the lowering of operating temperatures will offer even greater possibilities to the ice industry as a whole through increased operating efficiency.

2. *Field Investigation.*—A more specific example of the possibilities offered by the application of effective methods of air agitation is perhaps to be found in a summary of work recently conducted at the plant of the Suburban Ice Company located at La Grange, Illinois.

3. *Difficulties Previously Encountered at La Grange.*—The difficulties encountered at La Grange are basically attributable to the quality of water locally available. An analysis of the local well water is shown in Table 16, while the result of lime and alum treatment in a continuous cold lime softener is shown in Table 17. The total dissolved salts are not only comparatively high but the concentration of calcium sulphate is sufficiently great to cause the production of opacity due to the occurrence of an eutectic mixture if either marked localized or homogeneous concentration occurs.

The difficulties resulting from the quality of water available were further increased due to the fact that, in order to reduce the operating

TABLE 16

ANALYSIS OF CITY WATER AVAILABLE AT PLANT OF SUBURBAN ICE COMPANY, LA GRANGE, ILLINOIS

Ionic Constituents		Concentration, parts per million
Sodium	Na	32
Calcium	Ca	188
Magnesium	Mg	76
Chloride	Cl	45
Sulphate	SO_4	417
Carbonate	CO_3	219
Hypothetical Combinations		
Calcium carbonate	$CaCO_3$	364
Calcium sulphate	$CaSO_4$	147
Magnesium sulphate	$MgSO_4$	382
Sodium sulphate	Na_2SO_4	10
Sodium chloride	NaCl	74
Aluminum and iron oxides	R_2O_3	0.6
Silica	SiO_2	7
Suspended matter		12
Total dissolved solids		997

TABLE 17

ANALYSIS OF TREATED CITY WATER USED IN FREEZING PROCESS AT PLANT OF SUBURBAN ICE COMPANY, LA GRANGE, ILLINOIS

Ionic Constituents		Concentration, parts per million
Sodium	Na	23
Calcium	Ca	109
Magnesium	Mg	22
Chloride	Cl	15
Sulphate	SO_4	358
Carbonate	CO_3	96
Hydroxide	OH	1.2
Hypothetical Combinations		
Calcium carbonate	$CaCO_3$	16
Calcium sulphate	$CaSO_4$	348
Magnesium hydroxide	$Mg(OH)_2$	2
Magnesium sulphate	$MgSO_4$	106
Sodium sulphate	Na_2SO_4	41
Sodium chloride	NaCl	25
Silica	SiO_2	7
Total dissolved solids		545

Note: This represents an extremely effective lime and alum treatment. It should be noted that the combined calcium carbonate and magnesium hydroxide amount to only 18 parts per million.

TABLE 18

DISTRIBUTION OF POWER LOAD AT LA GRANGE ICE PLANT

Hp.	R.P.M.	Pulley in.	Driving	Pulley ft.	R.P.M.	Pressures lb.	Est. hp. Output	Est. Av. Kw. Demand
150	580	21.5	14 in. x 28 in. comp.	14	63	20–170	113.4	94.0
75	690	15.0	12 in. x 24 in. comp.	12	75	20–170	77.9	66.0
30	1145	10.0	6 in. x 6 in comp.	5	200	.....	....	....
20	860	14.5	12 in. x 8 in. comp.	3¾	300	10	18.2	16.0
20	860	14.5	12 in. x 8 in. comp.	3¾	300	10	14.8	13.0
20	1740	Direct	Centrifugal water pump	..	1740	21.7	16.4	14.4
15	860	6.5	5 in. x 36 in. deep well pump	3¼	22	20	7.8	7.0
			Tank Room				5.6	5.6
			Lights				2.7	2.0
			Yard				0.0	0.0
							256.8	218.0

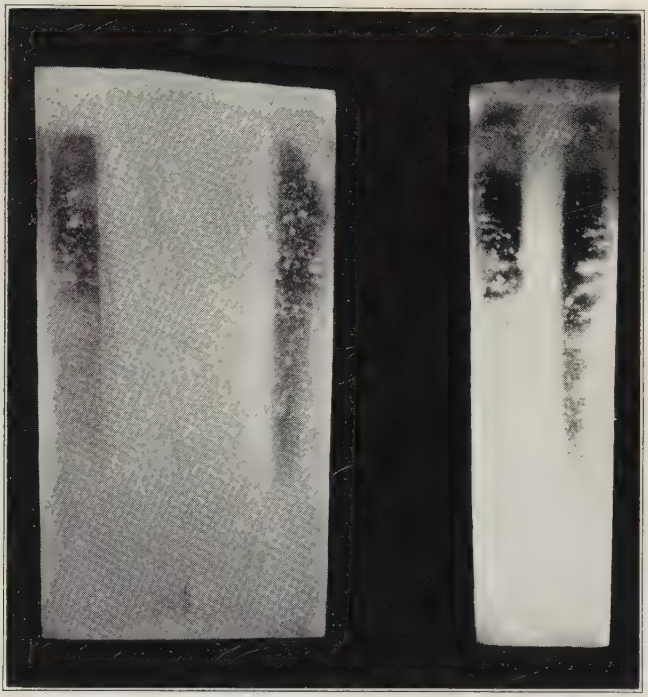

FIG. 43. ICE PRODUCED AT LA GRANGE, ILLINOIS, USING LOW PRESSURE AIR

expense of the plant, the medium pressure air formerly used for agitation was replaced by low pressure air produced by means of blowers. The reason for this change was occasioned by the fact that the 29-kw. power demand, if the two air compressors were utilized during the entire evening peak, was greater than 5 per cent of summer demand. It was desirable not to exceed this 5 per cent during winter evenings because of special discounts allowed by the power company. The 880 cans of the plant were, therefore, agitated by means of 410 cu. ft. of free air per minute, supplied at 2 pounds pressure (gage) with a 5.6-kw. demand. The allocation of the power demands of the plant is shown in Table 18.

The production occasioned by the low pressure air was entirely unsatisfactory. Samples of the average production are shown in Figs. 43, 44, and 45. This ice was produced in standard 300-lb. cans to which 1.12 cu. ft. of air for 1 hour and 0.45 cu. ft. of air for the remaining 47 hours of the freezing period was applied, the auxiliary air being applied by means of a straight piece of copper tubing hung over

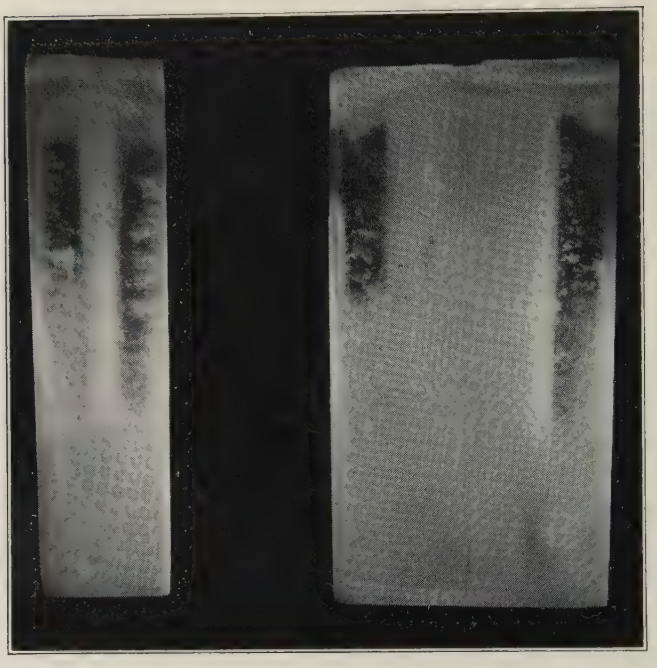

FIG. 44. ICE PRODUCED AT LA GRANGE, ILLINOIS, USING LOW PRESSURE AIR

the edge, the regular air by means of a standard straight side low-pressure drop tube. The average freezing temperature at the plant was 16 deg. F. If the brine temperature was lowered below this point an even more unsatisfactory product resulted. At 16 deg. F., however, the required tonnage could not be produced.

The effect of this production upon the plant's trade has become increasingly critical. The total production during 1929 has decreased greatly not only because the present product is entirely undesirable, but also because the local company is being threatened with active competition from clear ice produced from Lake Michigan water.

4. *Preliminary Investigation.*—A preliminary investigation indicated that the low pressure air did not afford sufficiently positive agitation to insure satisfactory operation, and arrangements were made to conduct a series of experimental runs at the plant wherein use could be made of high pressure air effectively applied. A row of twenty cans was, therefore, set aside for experimental purposes.

A decided attempt was made throughout the investigation to utilize as much of the present freezing equipment as possible. In order to

FIG. 45. ICE PRODUCED AT LA GRANGE, ILLINOIS, USING LOW PRESSURE AIR

use the present cans and still effect efficient side agitation during the first hours of the freezing period wherein the freezing rate is high and the tendency for localized concentration great, a number of auxiliary air headers were constructed which could be placed in the cans for the first hours of the freezing operation and supplied with a large volume of air during this period. These would be subsequently replaced by standard air tubes which could be frozen into the ice blocks according to standard procedure and would afford sufficient agitation with a much smaller volume of air after a sufficient layer of ice had been formed. The different types of auxiliary headers used are shown in Fig. 46. They were constructed from ¼-in. copper tubing and standard galvanized pipe fittings. The bottom headers were all perforated by means of a No. 64 drill, the holes being spaced 1 in. apart.

It is obvious that this type of auxiliary header cannot be allowed to become frozen into the ice cake at any time or even to be touched by the encroaching layer of ice. The whole effectiveness of the auxiliary header consists in its ability to be removed from the can as soon

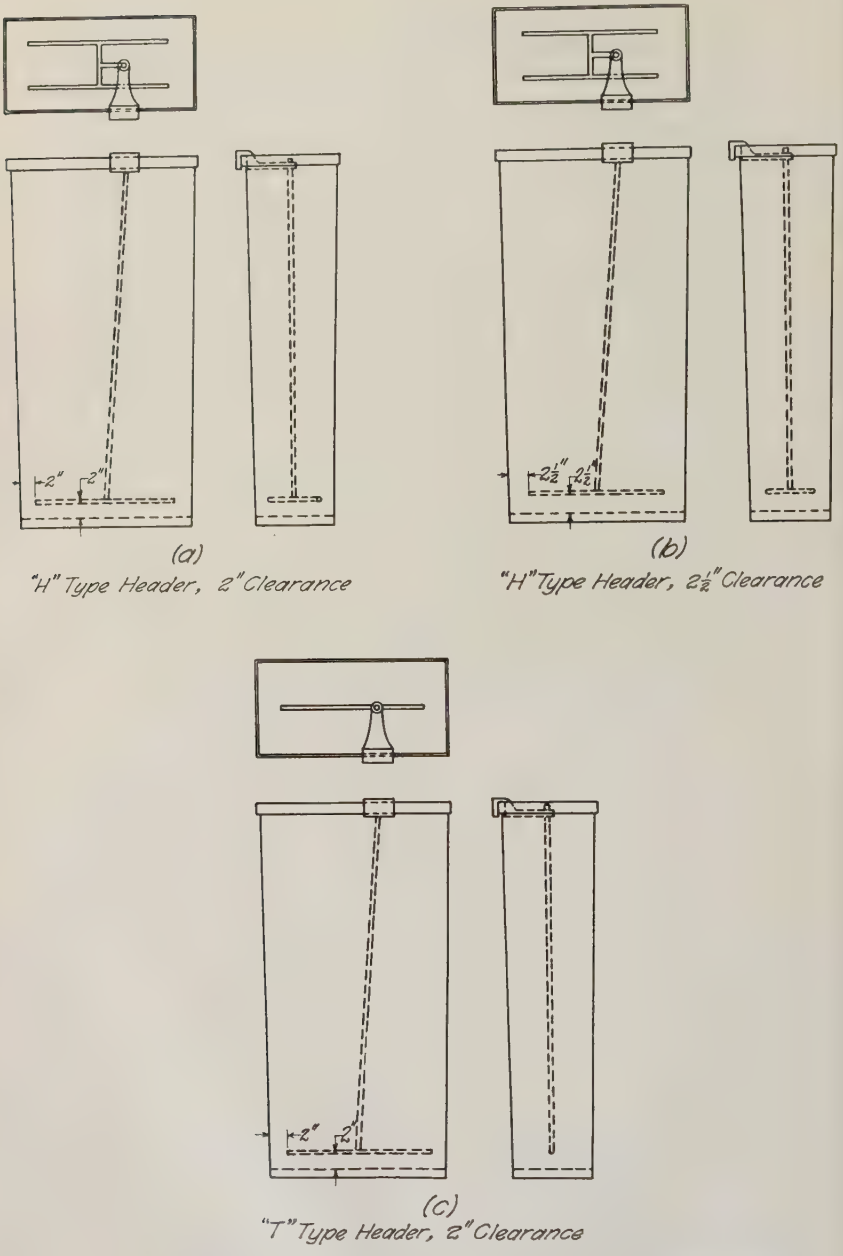

FIG. 46. TYPES OF AUXILIARY AIR HEADERS USED IN EXPERIMENTAL INVESTIGATION AT LA GRANGE, ILLINOIS

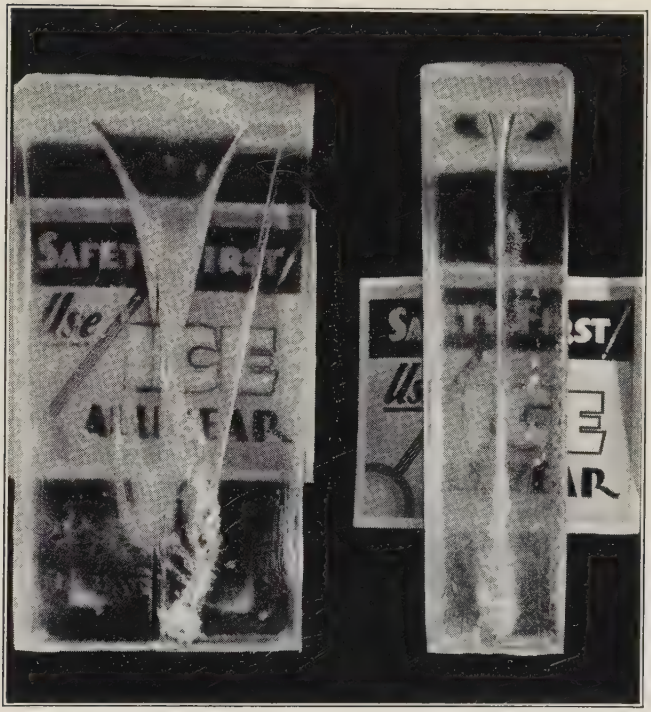

FIG. 47. ICE FROZEN FROM LA GRANGE WATER USING H TYPE AUXILIARY AIR HEADER

as the need for the auxiliary air agitation no longer exists. In operation the use of such headers requires careful manipulation and attention, since, if once touched by the ice layer, the header becomes embedded in the block and cannot be removed. This results in the ruining not only of the block but possibly of the header itself in being removed from the frozen cake. It is apparent that the T-type header shown in Fig. 46c possesses the most distinct advantages from the standpoint of these difficulties and, should its use prove sufficiently effective, would be the most desirable for plant use of the three types shown.

Several types of drop tubes were investigated by means of which the regular air supply, after the auxiliary headers had been removed, could be delivered to the cans. These consisted of the short straight-sided drop-tube type now used in the plant, and shown in Fig. 4b, the long straight-sided drop-tube type, which is similar to the latter except that the tube reaches to within 2 in. of the bottom of the can, and the so-called side drop-tube type shown in Fig. 4a.

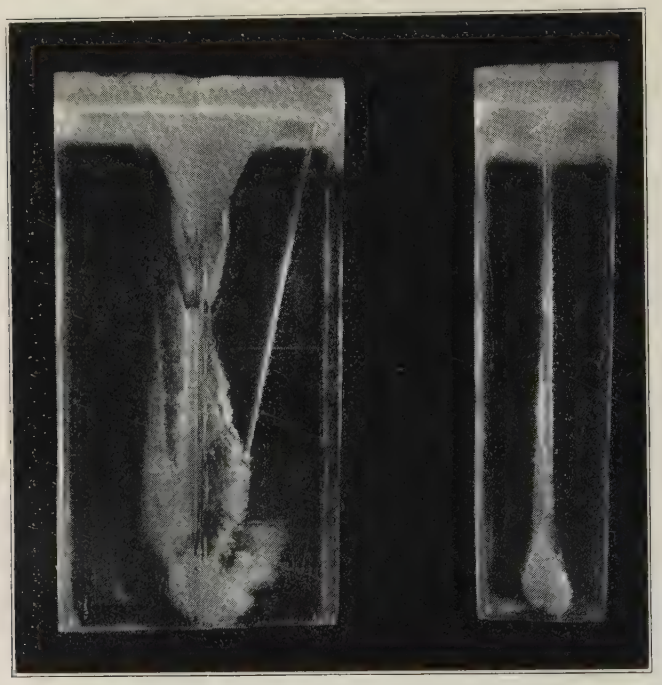

FIG. 48. ICE FROZEN FROM LA GRANGE WATER USING H TYPE AUXILIARY AIR HEADER

In the case of all experimental runs the air was connected to the auxiliary header in the can before the latter was immersed in the brine. This procedure follows as a result of the consideration developed in Appendix A.

5. *Results of Experimental Runs.*—The results of the experimental runs made to determine the relative effectiveness of the different types of auxiliary headers are shown in Figs. 47 to 52 inclusive, the conditions of the run being stated in Table 19.

An examination of the photographs and actual observation of the ice produced in each case lead to the following conclusions:

(1) Efficient air agitation at the sides of the can as afforded by a perforated auxiliary header is necessary. The same volume of air applied to single outlet tubes is ineffective in preventing the formation of an opaque shell encasing the lower sides of the frozen block.

(2) The T-type auxiliary header, which possesses many operational advantages, is entirely as effective in preventing side opaqueness as the H-type header.

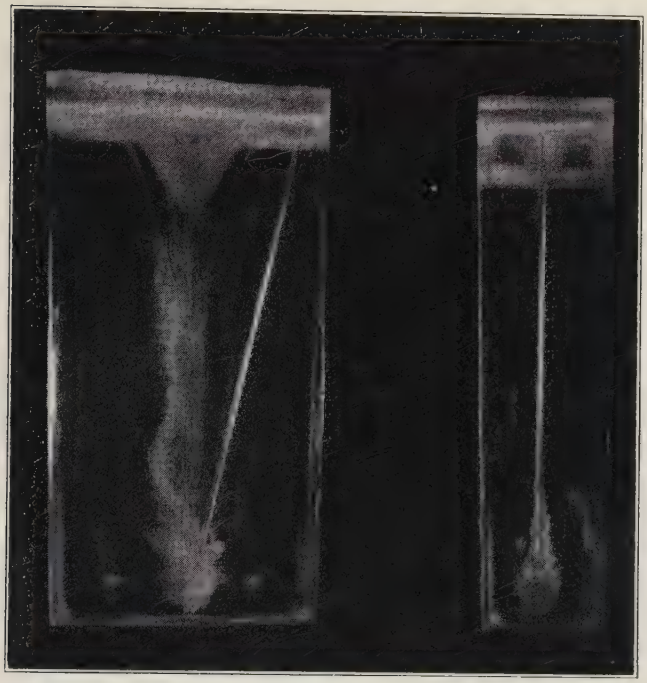

FIG. 49. ICE FROZEN FROM LA GRANGE WATER USING T TYPE AUXILIARY AIR HEADER

When the medium-pressure air agitation system at the plant was discarded in 1928 the two motor driven 12-in. x 8-in. compressors were retained. Obviously, the most desirable utilization of the compressors would be to operate only one unit and to allow the other to serve as standby equipment, to be used in case of emergency.

Using 1.3 cu. ft. of auxiliary air per min. for 1 hour and 0.3 cu. ft. of regular air per min. for the remaining 41 hours of an assumed 42-hr. freezing period, the average consumption of air per can is 0.325 cu. ft. per min. The total air required to agitate the 880 cans in the plant would thus be 286 cu. ft. per min. This requirement cannot be delivered by a single 12-in. x 8-in. compressor even though it were operated at maximum speed, the maximum capacity for such a machine at 300 r.p.m. being approximately 260 cu. ft. of free air per min. If, however, it could be determined that a smaller volume of regular air would still produce a suitable quality of ice, a single compressor might be utilized.

Several runs were therefore made in which 1.3 cu. ft. of air per min.

FIG. 50. ICE FROZEN FROM LA GRANGE WATER USING AUXILIARY AIR FOR AGITATION

The air was applied by means of a standard drop tube of the type shown in Fig. 4a.

was delivered to a T-type auxiliary header for 2 hours. By the end of this period an ice layer of sufficient thickness should have been formed at the sides of the can to permit efficient agitation by 0.1 cu. ft. of air per min. for the remaining 40 hours of the freezing period. Under such conditions the average air requirements per can would be 0.157 cu. ft. per min., and the total air required in the plant 880 x 0.157 or 138 cu. ft. per min. This volume of air could readily be supplied by a single 12-in. x 8-in. compressor. The result of freezing the La Grange water under these latter conditions of air agitation is shown in Fig. 53. The brine temperature in this case was 13 deg. F., the auxiliary air was supplied to a T-type auxiliary header, and the regular air to the side drop tube type shown in Fig. 4a. The product is seen to be comparable to that produced using the larger total volume of air for agitation.

It has been emphasized that the low-pressure-blower system was originally installed in order to afford a peak load demand which would be less than 5 per cent of the maximum demand of 218 kw. and which

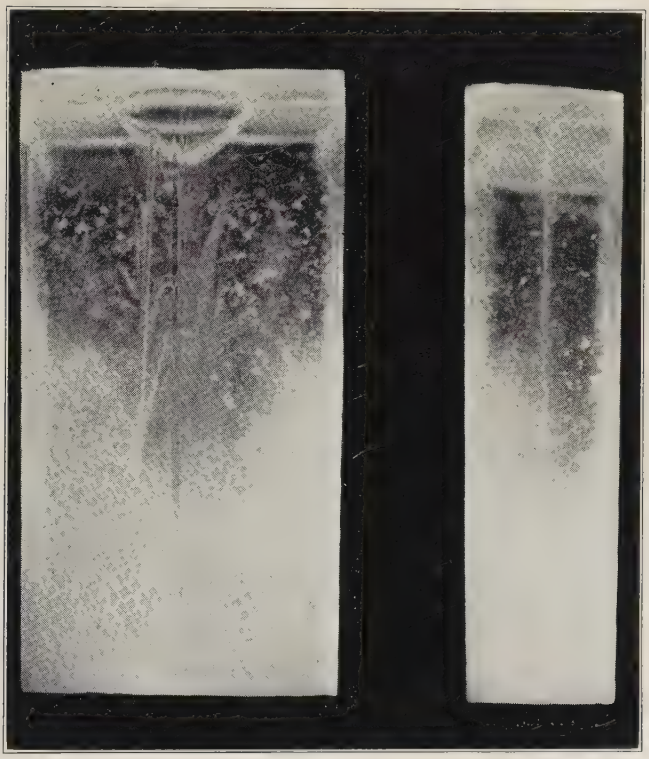

FIG. 51. ICE FROZEN FROM LA GRANGE WATER USING AUXILIARY AIR FOR AGITATION

The air was applied to a short straight-sided standard drop tube of the type shown in Fig. 4b.

would thus insure the greatest saving on the yearly power bill. If the blower were to be replaced by a single 12-in. x 8-in. compressor operating at 30 lb. (gage) and delivering the necessary 138 cu. ft. of air per min. to the air laterals at 20 lb. (gage) the power demand would be 15 h.p. or 11.2 kw. This is seen to be somewhat greater than the 10.9 kw. load representing 5 per cent of the maximum summer demand, and below which the plant must operate in order to obtain the minimum rate. The necessity for this minimum power demand exists during the evenings of the four winter months during which the demand for ice is at a minimum. In 1929 the plant actually operated only a fraction of one month during this period. Consequently, during this time a large portion of the 880 cans in the plant are completely frozen and require no air supply. No data are available as to what per cent of the cans are frozen during this period. It

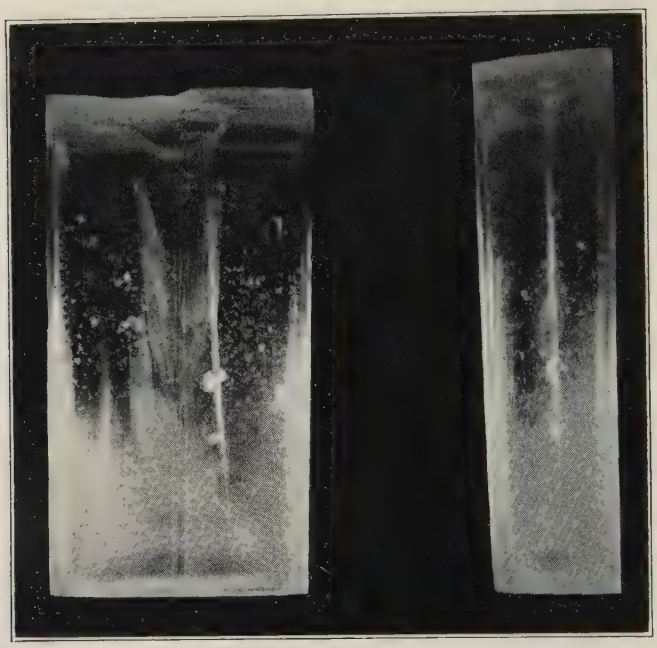

FIG. 52. ICE FROZEN FROM LA GRANGE WATER USING AUXILIARY AIR FOR AGITATION

The air was applied to a long straight-sided standard drop tube of the type shown in Fig. 4b.

seems safe to assume, however, that the power demand for air agitation will be actually below 10.9 kw., since only a fraction of the plant's maximum production is required during these four months to supply current needs.

The cost of high-pressure air agitation utilized as proposed may be calculated by assuming an average brine temperature of 14 deg. F., which will result in an average freezing time of 42 hours and an average production of 75 tons per day. If the power demand for air agitation is 11.2 kw. the power cost per ton is

$$\frac{24 \times 11.2}{75} \text{ or } 3.6 \text{ kw.}$$

3.6 kw. at \$0.015 = \$0.054 per ton of ice produced. The present low-pressure air requirements of 410 cu. ft. of air per min. for the 880 cans of the plant requiring a demand of 5.6 kw. amounts to \$0.03 per ton of ice produced.

The greatest disadvantage inherent in any type of removable auxiliary air headers lies in the added labor required in the installation and

Table 19

Conditions Existing During Experimental Runs Made to Determine Relative Effectiveness of Different Types of Auxiliary Air Headers

Ice Shown in Fig.	Type of Auxiliary Header	Amount of Auxiliary Air Used cu. ft. per min.	Duration of Auxiliary Air Agitation hr.	Type of Regular Air Tube	Amount of Regular Air Used cu. ft. per min.	Brine Temperature deg. F.	Number of Cores Removed	Amount of Core Water Removed	Total Freezing Time hr.
47	H Type 2 in. Clearance	1.3	1	Side Drop Tube see Fig. 9	0.3	14	2	7 gallons (=19%) ½ gallon	42
48	H Type 2½ in. Clearance	1.3	1	Side Drop Tube see Fig. 9	0.3	14	2	7 gallons (=19%) ½ gallon	42
49	T Type	1.3	1	Side Drop Tube see Fig. 9	0.3	14	2	7 gallons (=19%) ½ gallon	42
50	Side Drop Tube	1.3	1	Side Drop Tube see Fig. 9	0.3	14	2	7 gallons (=19%) ½ gallon	42
51	Short Straight Drop Tube	1.3	1	Short Straight Drop Tube	0.3	14	2	7 gallons (=19%) ½ gallon	42
52	Long Straight Drop Tube	1.3	1	Long Straight Drop Tube	0.3	14	2	7 gallons (=19%) ½ gallon	42

FIG. 53. ICE FROZEN FROM LA GRANGE WATER IN STANDARD 300-LB. CAN USING T TYPE AUXILIARY AIR HEADER

Air was supplied at the rate of 1.3 cu. ft. of air per min. for 2 hours followed by 0.1 cu. ft. of air per min. for the remainder of the run.

removal during each run, and particularly in seeing that they do not become frozen into the block of ice. In the operation of the new type of ice can previously described in Fig. 12, Chapter II, both of the disadvantages inherent in the removal header are overcome. No extra labor is required, and the danger of freezing into the block is removed completely.

In order to indicate the quality of product which may be expected when the La Grange water is frozen in this can, a run was made in which the brine temperature was 13 deg. F., and the amount of air used for agitation was 1.3 cu. ft. per min. for two hours, followed by 0.1 cu. ft. per min. for the remaining 40 hours of the run. The resulting product is shown in Fig. 54 and is seen to be entirely comparable to that shown in Fig. 53.

FIG. 54. ICE FROZEN FROM LA GRANGE WATER IN NEW TYPE OF ICE CAN

6. *Summary.*—A summary of the La Grange investigation leads to the following conclusions:

(1) Without altering the operation of the water treating equipment now being used it is possible to produce a desirable and marketable quality of ice when the local water is frozen at brine temperatures sufficiently low to produce the maximum daily tonnage required.

(2) Ice of a highly marketable grade can be produced at the plant if certain changes are made in the operating procedure, the chief of which entails the installation of a high-pressure air system for agitation.

(3) Using a removable T-type auxiliary air header, utilizing 1.3 cu. ft. of free air per min. for 2 hours, replaced at the end of this time by a side drop tube to which 0.1 cu. ft. of free air per min. is supplied for the remainder of the run, a marketable product can be produced.

(4) If the same amount of air as described under (4) is used in the new type of ice can described in Chapter II, a product of comparable quality is produced. The new type of can possesses the following advantages: (a) no extra labor is required to insert and remove the auxiliary header, and (b) the danger of having the auxiliary header frozen into the ice cake is removed.

(5) In order to produce the desirable quality of ice referred to under (4) as being possible at La Grange, two cores must be removed, one of 8 gallons, followed later in the freezing process by a second of ½ gallon. The power loss incurred in such procedure has been shown to amount to only 0.15 per cent of the total production cost.

(6) None of the proposed changes over the present operational procedure are felt to incur any marked increase in production cost. The actual cost of the power required for agitation under the high pressure system, amounting to $0.05 per ton, compares favorably with that of $0.03 per ton required in the low pressure system now being used.

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